This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

QUALITATIV
CHEMICAL ANALYSIS

A. A. NOYES

44
N9[illegible]
ic

LELAND·STANFORD·JVNIOR·VNIVERSITY

QUALITATIV CHEMICAL ANALYSIS

A. A. NOYES

A COURSE OF INSTRUCTION
IN THE
QUALITATIV CHEMICAL ANALYSIS
OF INORGANIC SUBSTANCES

BY

ARTHUR A. NOYES

PROFESSOR OF THEORETICAL CHEMISTRY IN THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SIXTH EDITION

STANFORD LIBRARY

NEW YORK:
THE MACMILLAN COMPANY.
LONDON: MACMILLAN & CO., LTD.
1915

Cr.

Copyright, 1915
By Arthur A. Noyes

246106

PREFACE.

This text-book is an attempt, on the experimental side, to train the student of qualitativ analysis in careful manipulation and exact methods of procedure, such as are commonly employed in quantitativ analysis. It is an attempt, on the theoretical side, to make clear to the student the reason for each operation and result, and to accustom him to apply to them the laws of chemical equilibrium and the principles relating to the ionization and complex-formation of substances in solution. It is believed that in both these ways the educational value of the subject is greatly increased.

The book is divided into two main Parts, entitled The Course of Instruction and The System of Analysis. In presenting the System of Analysis the plan adopted in the earlier editions of this book has been followed, namely, that of separating sharply the description of the operations from the discussion and explanation of them. The operations are described with as great definitness as possible in short paragraphs entitled "Procedures"; and each of these is followed by "Notes" in which are given the reasons for the operations, the precautions necessary and difficulties encountered in special cases, the chemical behavior of the different elements, the indications afforded of their presence, and the application of the theoretical principles to the reactions involved. The system of procedure has been thoroly revised as a result of the extended investigations made in the laboratory of this Institute during the past six years and described in volumes 29, 30, 31, and 34 of the Journal of the American Chemical Society. As a result of these investigations, in which the author has had the able cooperation of Professor W. C. Bray and Professor E. B. Spear, the process of analysis has been made much more reliable, so that now it is possible with careful manipulation to detect one milligram of any constituent in the presence of 500 milligrams of any other (except in a few combinations where the limit of detectability is two milligrams). At the same time the process has on the whole been considerably simplified. The larger size of the present edition is due, not to greater complexity of the process, but to the inclusion in the Procedures of the more explicit directions necessary to secure accuracy in the separations and reactions, to the insertion of confirmatory tests for most of the elements, to the development of a more systematic process for the detection of the acidic constituents, and to the elaboration of the notes and especially the inclusion in them of the theoretical explanations made possible by the recent development of our knowledge of solutions.

The Course of Instruction includes two sections—one entitled Laboratory Experiments, giving the directions for the laboratory work; and the other entitled Questions on the Experiments, consisting of a series of questions to be studied in connection with the class-room exercises.

The laboratory work described in the section on Laboratory Experiments is from beginning to end closely correlated with the systematic scheme of analysis. For experience has convinced the author that the plan followed in many textbooks of requiring the student to study the separate reactions characteristic of the various elements before undertaking their systematic separation is highly unsatisfactory. However valuable the knowledge of the additional reactions may be, it is found in practis that the performance of such a large number of independent, disconnected experiments makes little impression on the student's mind and fails to awaken his interest in the subject. Qualitativ analysis affords an effectiv means of teaching a part of inorganic chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because the student sees a practical use of the information presented to him; but these advantages evidently do not apply to facts not directly related to the process of analysis.

The Questions on the Experiments are intended to aid the student in understanding the work that he is doing in the laboratory and to make sure that he derives from the subject the mental traning which it ought to afford. The questions are in large part of such a character that, in order to answer them properly, the student not only must study the Notes on the Procedures, but also must giv to the questions some independent thought. It is assumed in these questions, as well as in the Notes on the Procedures, that the student has acquired, in his previous course on Inorganic Chemistry, a general knowledge of the mass-action law and of the chemical aspects of the ionic theory.

The best plan of conducting the course, when circumstances permit, is in the author's opinion as follows: The class, if large, is divided into sections of from 15 to 25 students. At the beginning of each laboratory exercise, which should, if possible, be three hours long, or at the beginning of every second laboratory exercise, the instructor holds a class-room conference with each section, at which the experiments to be next made are discussed in outline, and those made at the previous exercises are reviewed in detail. The conferences are carried on mainly by questioning the individual students and by encouraging them to ask questions as to matters which they do not understand. As preparation for each conference the student is expected to study the Table in which is presented the outline of the analysis of the group to be next taken up, to study the Notes on the Procedures which he has worked through just previously in the laboratory, and (unless the course is an elementary one) to answer the questions on the corresponding Experiments. To ensure that the student givs proper study to the subject, a short written exercise may well be held at the beginning of each conference. In the laboratory work the class may be kept nearly together by giving to the faster working students additional unknown solutions on each group, and by allowing those who are falling behind to omit some of the less important Experiments. In the laboratory great stress is laid on careful work, such as will enable the proportions of the various constituents present in unknown solutions to be estimated and small quantities of them to be detected. An effectiv means of teaching the details of manipulation is for the instructor to carry through in the lecture-room, after the students have had a little experience of their own in the laboratory, the complete process for the analysis of the copper-group.

Even when the time available for the subject of qualitativ analysis does not permit of so complete a course as that here presented, the student gets, in the author's opinion, a better training by working through selected parts of an exact scheme of analysis carefully and thoroly than he does by covering the whole of an elementary scheme superficially. Experiments that may be well omitted in briefer courses are indicated by asterisks prefixed to the description of them in the section entitled Laboratory Experiments.

PREFACE TO THE FIFTH EDITION.

In this edition important changes and additions have been made as follows. The Procedures for the detection of the basic constituents and the Notes upon them have been improved in many matters of detail; and there have been introduced a simpler process for the detection of nickel and cobalt and a more satisfactory one for the analysis of the alkali-group. The part of the book relating to the detection of the acidic constituents has been entirely rewritten; and a more complete and more instructiv system of analysis for those constituents has been presented. Many additional tabular outlines have been included to assist the beginner in grasping the general plan of the separations; and the Questions on the Experiments have been revised.

In making this revision the author has had the benefit of many valuable suggestions from Professors Henry Fay, W. T. Hall, and A. A. Blanchard of this Institute, and from Prof. G. S. Forbes of Harvard University.

PREFACE TO THE SIXTH EDITION.

The main changes in this edition are modifications of the detailed directions for some of the Procedures, suggested by further experience with them, and the inclusion of a comprehensiv Index, for the preparation of which I am greatly indebted to Mr. Roger Williams.

ARTHUR A. NOYES.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, August, 1915.

TABLE OF CONTENTS.

PART I. THE COURSE OF INSTRUCTION. PAGE

LABORATORY EXPERIMENTS 1
QUESTIONS ON THE EXPERIMENTS 13

PART II. THE SYSTEM OF ANALYSIS.

PREPARATION OF THE SOLUTION 27
DETECTION OF THE BASIC CONSTITUENTS 41
DETECTION OF THE ACIDIC CONSTITUENTS 94

APPENDICES.

PREPARATION OF THE REAGENTS 117
PREPARATION OF THE TEST-SOLUTIONS 120
APPARATUS REQUIRED 122
IONIZATION-VALUES 123
ATOMIC WEIGHTS OF THE COMMON ELEMENTS 124
SOLUBILITIES OF SLIGHTLY SOLUBLE SUBSTANCES 124

INDEX 126

LIBRARY

PART I.

THE COURSE OF INSTRUCTION.

LABORATORY EXPERIMENTS.

DETECTION OF THE BASIC CONSTITUENTS.

Preliminary Work.—Check off on an apparatus slip (corresponding to that printed on page 122) the apparatus found in the desk, and sign and hand in the slip.

Make a 750 cc. wash-bottle, taking pains to bend the tubes and to cut them off so as to correspond closely with the model exhibited in the laboratory. Make also a 250 cc. wash-bottle (for washing with hot water and special solutions).

Make a dropper about 10 cm. (4 inches) long by drawing out one end of a glass tube to a fairly wide capillary and slightly expanding the other end with the aid of a file while it is heated in a flame. Cap the expanded end with a rubber nipple.

Make 3 stirring-rods about 15 cm. long by cutting a piece of glass rod into sections and then rounding the ends in a flame.

Experiment 1.—*Separation of the Basic Constituents into Groups.*—In connection with this experiment read the General Discussion on page 41 and refer to Table II (page 42). Measure out with the aid of a 10 cc. graduate 5 cc. portions of the test-solutions (see Note 1) of $AgNO_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, and KNO_3. Mix the portions in a conical flask, add 5 cc. 6-normal HNO_3 and 10 cc. NH_4Cl solution, shake for a minute or two, and filter. Dilute the filtrate with water to a volume of 100 cc. Place it in a 200 cc. conical flask; insert a two-hole rubber stopper through which passes a tube leading to the bottom; and pass in a slow current of H_2S, until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of it. Filter. To the filtrate add 10 cc. NH_4OH and 3–5 cc. $(NH_4)_2S$. Shake the mixture and filter. Evaporate the filtrate to a volume of about 10 cc., filter, and to the cold solution add 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. alcohol.

In this experiment and all subsequent ones observe carefully everything that happens, and record it clearly and neatly in the note-book in the way described in Note 2, together with the equations expressing all the chemical changes that take place. In connection with each Experiment study the Table and the Notes referred to in the directions.

Notes.—1. The solutions of constituents to be tested for, here called the test-solutions, are all so made up as to contain 10 mg. (10 milligrams) of the constituent per cubic centimeter of solution. The mixture used in this experiment therefore contains 50 mg. of each of the basic constituents silver, copper, zinc, calcium, and potassium. The student should acquire the habit of working with definit quantities of the constituents and of noting the size of the precipitates which they yield. For a good qualitativ analysis should not only show the presence or absence of the various constituents, but should also furnish an estimate of the proportions in which they are present.

Test-solutions should not be used in place of reagents, nor reagents in place of test-solutions, since the concentrations are as a rule quite different. In regard to the concentrations of reagents, see Note 3, page 44.

2. In the note-book the operations should be indicated very briefly; but everything that happens should be recorded fully, tho concisely. Thus the report of the first experiment may be made in the following form:

Expt. 1.—Added HNO_3: no change observed.
Added NH_4Cl: white curdy ppt.
$Ag^+NO_3^- + NH_4^+Cl^- = \underline{AgCl} + NH_4^+NO_3^-$.
Passed in H_2S: large black flocculent ppt.
$Cu^{++}(NO_3^-)_2 + H_2S = \underline{CuS} + 2H^+NO_3^-$.

. . . .

Solid substances involved in chemical reactions should be indicated by underlining their formulas. Largely ionized dissolved substances should be written with + and — signs attached to the formulas in such a way as to show the ions into which they dissociate. Slightly ionized dissolved substances should be distinguished by not attaching these signs to the formulas. In regard to the ionization of substances, see the Table on page 123.

The neatness, accuracy, and completeness of the notebook record will be an important factor in determining the grade of the student.

Experiment 2.—*Analysis of the Silver-Group.*—Mix in a conical flask 20 cc. of the test-solution of $Pb(NO_3)_2$ with 5 cc. portions of the test-solutions of $Bi(NO_3)_3$, $AgNO_3$, and $Hg_2(NO_3)_2$, and treat the mixture by P. 11–15 (*i.e.*, by Procedures 11–15 of the System of Analysis described in Part II, on pages 43–46); omit the confirmatory tests mentioned at the end of P. 12 and 13. Study Table III (page 43) before carrying out this experiment; and in connection with it read the Notes on P. 11–15.

Note.—In all these "Experiments" only the Procedures actually named in the directions should be worked through, omitting any others that may be incidentally referred to in the System of Analysis.

Experiment 3.—*Precipitation by Hydrogen Sulfide.*—To 10 cc. of the test-solution of $Bi(NO_3)_3$ in a 200 cc. conical flask add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 75 cc. water; and, without filtering the mixture, pass H_2S into it till it becomes saturated, in the way described in the first paragraph of p. 21, omitting the filtration at the end. (The HNO_3 and NH_4Cl are added and the solution is diluted to 100 cc. so as to have the same conditions as in an actual analysis.)—Read Notes 1 and 2, P. 21.

*To 10 cc. of the test-solution of H_3AsO_4 add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 75 cc. water. Treat this solution by the whole of P. 21.—Read Note 3, P. 21.

* *Note.*—Experiments or parts of experiments preceded by an asterisk may be omitted in brief courses on the subject when the instructor so directs.

Experiment 4.—*Effect of Acid on the Precipitation by Hydrogen Sulfide.*—Introduce into each of three test-tubes by means of a dropper (see Note 2, P. 11) 3 drops of the test-solution of $Cd(NO_3)_2$. Add to the first tube 1 cc. HCl, to the second 3 cc. HCl, and to the third 9 cc. HCl. Then add to each solution enough water to make the volume about 20 cc., and pass a slow current of H_2S into it for about a minute.—Repeat the last test (with 9 cc. HCl), substituting $Cu(NO_3)_2$ for the $Cd(NO_3)_2$.—Calculate the normal concentration of the HCl in each tube and the number of milligrams of cadmium or copper per 100 cc. solution; and record the values in the note-book.—Read Notes 4 and 5, P. 21.

Experiment 5.—*Effect of Oxidizing Substances on Hydrogen Sulfide.*—To 20 cc. of the test-solution of $Fe(NO_3)_3$ add 10 cc. NH_4Cl solution, 5 cc. HNO_3, and 65 cc. water, and pass in H_2S till the solution is saturated. Repeat this experiment, substituting 20 cc. of the test-solution of K_2CrO_4 for that of the $Fe(NO_3)_3$.—Read Notes 6 and 7, P. 21.

Experiment 6.—*Analysis of the Copper-Group.*—Mix 10 cc. portions of the test-solutions of $Hg(NO_3)_2$, $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$, add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 35 cc. water, treat the mixture by P. 21, and treat the precipitate so obtained by P. 31–38.—Refer to Table V (page 54), and read the Notes on P. 31–38.

Experiment 7.—*Analysis of an Unknown Solution for Elements of the Copper-Group.*—Ask the instructor for an unknown solution containing elements of the copper-group ("unknown *A*"), and analyze 10 cc. of it by P. 21 and P. 31–38, first adding 5 cc. HNO_3 and 10 cc. NH_4Cl solution. Record and report the results as described in the following Note. Keep all final tests in properly labelled test-tubes or flasks until the report on the analysis has been returned by the instructor.

Note.—Record the results of the analyses of unknown solutions in the notebook in three columns headed respectivly, "Operations," "Observations," "Conclusions." The operations and observations are to be recorded in the same brief form employed in the experiments with known solutions. In the column headed Conclusions are to be inserted the conclusions that may be drawn from each observation as to the presence or absence of any of the constituents that may be present in the unknown solution. The chemical equations involved need not be written. Sum up at the end the constituents that have been found to be present, giving also a rough estimate of the quantity of each of them per 10 cc. of solution. Quantities less than 5 mg. may be reported as "small"; those from 5 to 50 mg. as "medium"; and those greater than 50 mg. as "large." (It is to be noted, since one gram of a non-metallic solid substance is ordinarily taken for analysis, that 5 mg. corresponds to the presence of 0.5% and 50 mg. to the presence of 5% of the constituent in such a substance.) The quantity of any constituent present is to be estimated from the size of the precipitate obtained in the confirmatory test or in the Procedure preceding it. The student should make it a habit to compare this precipitate in any doubtful case with that obtained by subjecting a known quantity of the test-solution to the same final Procedure. For this purpose the test-solution may be measured out with the aid of a dropper, noting that three medium-size drops correspond to about 0.1 cc. of the solution or to 1 mg. of the constituent contained in it.—The instructor will return the report of the student with an entry upon it showing the quantities of the various constituents which the unknown actually contained.

The correctness of the results obtained in the analysis of these unknown solutions is an important factor in determining the grade of the student.

Experiment 8.—*Behavior of Elements of the Tin-Group towards Hydrogen Sulfide and Ammonium Sulfide.*—To 5 cc. water in each of three test-tubes add from a dropper 6 drops respectivly of the test-solutions of $AsCl_3$, of $SbCl_3$, and of $SnCl_4$. (Note that 6 drops of a test-solution contains 2 mg. of the constituent to be tested for.) Pass H_2S into each tube for half a minute. Then add from a graduate 2 cc. ammonium polysulfide solution. Finally add 3 cc. HCl slowly to each tube, and shake the mixture.—Compare these precipitates with that produced by mixing 5 cc. water, 2 cc. ammonium polysulfide solution, and 3 cc. HCl, and shaking. (In an actual analysis the analyst decides from the appearance of the HCl precipitate whether it contains an appreciable quantity of the tin-group.)—Refer to Table IV (page 47).

Experiment 9.—*Separation of the Tin-Group from the Copper-Group.*—To a mixture of 5 cc. portions of the test-solutions of $Bi(NO_3)_3$, $AsCl_3$, $SbCl_3$, and $SnCl_4$ add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and enough water to make the volume 100 cc. Treat the mixture by the first paragraph of P. 21, filter with the aid of suction (see Note 1, P. 23), treat the precipitate by P. 22, using 10 cc. ammonium polysulfide, reject the residue of Bi_2S_3, and treat the solution by P. 23. Treat at once the precipitate obtained in P. 23 as described in Expt. 10.—Refer to Table IV (page 47); and read the Notes on P. 22 and P. 23.

Experiment 10.—*Analysis of the Tin-Group.*—Treat the precipitated sulfides obtained in Expt. 9 by P. 41–46.—Refer to Table VI (page 60), and read the Notes on P. 41–46.

Experiment 11.—*Analysis of Unknown Solutions for Elements of the Copper and Tin Groups.*—Ask for two unknown solutions containing elements of these groups ("unknowns *B* and *C*"), and analyse 10 cc. of each of them. First, in order to secure the proper acid concentration for the H_2S precipitation, make the solution exactly neutral by adding to it NH_4OH drop by drop till it no longer reddens blue litmus paper, and add just 5 cc. HNO_3 and enough water to make the volume 100 cc. Then treat the mixture by P. 21–46. (Unknown *B* will contain only elements of the tin-group.)

Experiment 12.—*Precipitation of the Aluminum and Iron Groups and Solution of the Group-Precipitate.*—Treat a mixture of 10 cc. portions of the test-solutions of $Co(NO_3)_2$ and of $Fe(NO_3)_3$ by P. 51 and by the first five lines of P. 52.—Refer to Table VII (page 65), and read Note 1, P. 51, and Notes 1–2, P. 52.

Experiment 13.—*Behavior of Elements of the Aluminum and Iron Groups towards Ammonium Hydroxide and Sulfide.*—To 5 cc. portions of the test-solutions of $Al(NO_3)_3$, $CrCl_3$, $Fe(NO_3)_3$, $FeSO_4$, $Zn(NO_3)_2$, $Mn(NO_3)_2$, $Ni(NO_3)_2$, and $Co(NO_3)_2$, in separate test-tubes add 3 cc. NH_4Cl solution and 8–10 drops of NH_4OH, and note the result. Then add 2–3 cc. more NH_4OH. Finally add 1–2 cc. $(NH_4)_2S$ to each tube. Filter out the NiS precipitate, and boil the filtrate for 2 or 3 minutes. Record the results of all these tests in a single table, so as to show what effect is observed and what compound is formed in the case of each element upon the addition of each reagent.—Study the results, refer to Table VII, and read Notes 2–5 and 8–10, P. 51.

Experiment 14.—*Behavior of Elements of the Aluminum and Iron Groups towards Sodium Hydroxide and Peroxide.*—To separate 5 cc. portions of the test-solutions named in Expt. 13, add 8–10 drops of NaOH, and note the result. Then add 2–3 cc. more, and again note the result. Finally to each of the mixtures add gradually from a dry 7-cm. test-tube 0.2–0.3 cc. Na_2O_2 powder, and heat it to boiling. Record all the results in a single table as in Expt. 13.—Study the results, refer to Table VII, and read Notes 3–7, P. 52.

***Experiment 15.**—*Precipitation of Alkaline-Earth Elements by Ammonium Hydroxide in the Presence of Phosphate.*—Heat about

0.3 g. solid $Ca_3(PO_4)_2$ with 10 cc. water; then add 5 cc. HNO_3. To the solution add NH_4OH till the mixture after shaking smells of it; filter out the precipitate; and add 1–2 cc. $(NH_4)_2CO_3$ reagent to the filtrate.—Read Notes 6–7, P. 51, and Note 8, P. 52.

Experiment 16.—*Analysis of the Aluminum-Group.*—Treat a mixture of 10 cc. portions of the test-solutions of $Al(NO_3)_3$, $CrCl_3$, and $Zn(NO_3)_2$ by the second paragraph of P. 52 and by P. 53–57. Refer to Table VIII (page 71), and read the Notes on P. 53–57.

Experiment 17.—*Analysis of the Iron-Group: Separation of Manganese and Iron.*—Treat a mixture of 10 cc. portions of the test-solutions of $Mn(NO_3)_2$, $Fe(NO_3)_3$, $Zn(NO_3)_2$, $Co(NO_3)_2$, and $Ni(NO_3)_2$ by the second paragraph of P. 52; and treat the precipitate thereby obtained by P. 61, 62, 64, and 66. Treat the precipitate containing the zinc, cobalt, and nickel as described in Expt. 18.—Refer to Table IX (page 74), considering only the case where "phosphate is absent," and read the Notes on P. 61, 62, 64, and 66.

***Experiment 18.**—*Analysis of the Iron-Group: Separation of Zinc, Nickel, and Cobalt.*—Treat the residue and precipitate obtained in Expt. 17 by P. 67–70.—Refer to Table X (page 78), and read the Notes on P. 67–70.

Note.—In brief courses this experiment may be omitted; and in the subsequent analyses of unknowns cobalt and nickel may be detected (without distinguishing them) by the formation of a black precipitate in P. 66, and zinc may be tested for only in the aluminum-group.

***Experiment 19.**—*Modification of the Analysis of the Iron-Group in the Presence of Phosphate for the Purpose of Detecting Alkaline-Earth Elements.*—Mix together 10 cc. portions of the test-solutions of $Fe(NO_3)_3$, of $Co(NO_3)_2$, and of $Ca_3(PO_4)_2$ in HNO_3. Treat one-tenth of this solution by P. 63, and treat the remainder of it by P. 65 and 66. To the filtrate obtained in P. 66 add 2–3 cc. $(NH_4)_2CO_3$ reagent. —Read the Notes on P. 65.

Experiment 20.—*Analysis of Unknown Solutions for Elements of the Aluminum and Iron Groups.*—Ask the instructor for two unknown solutions for this purpose ("unknowns *D* and *E*"), and treat 10 cc. of each by P. 51–57 and 61–70. (Unknown *E* will contain phosphate.)

Experiment 21.—*Precipitation of the Alkaline-Earth Group.*—To 2 cc. of the test-solution of $Mg(NO_3)_2$ add 10 cc. water and 1–2 cc. $(NH_4)_2CO_3$ reagent, and shake the mixture for about a minute. Then add (in accordance with P. 81) 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. 95 per cent alcohol, and shake for a minute more.

To 2 cc. of the test-solution of $Ca(NO_3)_2$ add 10 cc. water and 2 cc. $(NH_4)_2CO_3$ reagent, shake, and after 2–3 minutes filter out the precipitate. To the filtrate add 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. 95 per cent alcohol.—Read the Notes on P. 81.

Experiment 22.—*Analysis of the Alkaline-Earth Group.*—Mix together in a small flask 3 cc. portions of the test-solutions of $BaCl_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$. Add to the mixture 30 cc. of the $(NH_4)_2CO_3$ reagent and 30 cc. 95 per cent alcohol, and shake it for about 5 minutes. Filter out the precipitate and treat it by P. 82–89. —Refer to Table XI (page 81), and read the Notes on P. 82–89.

Experiment 23.—*Analysis of the Alkali-Group.*—Mix together 10 cc. portions of the test-solutions of KNO_3 and $NaNO_3$, add 10 cc. NH_4Cl solution and 10 cc. $(NH_4)_2CO_3$ reagent, and treat the mixture by P. 91–95.—Refer to Table XII (page 87), and read the Notes on P. 91–95.

Experiment 24.—*Analysis of an Unknown Solution for Elements of the Alkaline-Earth and Alkali Groups.*—Ask the instructor for an unknown solution for this purpose ("unknown *F*"), and analyze 10 cc. of it by P. 81–89 and P. 91–95.

***Experiment 25.**—*Detection of Ammonium.*—Treat 0.2–0.3 g. solid NH_4Cl by P. 96.—Read the Notes on P. 96.

***Experiment 26.**—*Determination of the State of Oxidation of Iron.* —Treat 0.3 g. finely powdered Fe_3O_4 by P. 97, omitting tests *a*, *b*, and *c*.—Read the Notes on P. 97.

***Experiment 27.**—*Determination of the State of Oxidation of Arsenic.* —Treat 1 cc. of the test-solution of H_3AsO_4 by P. 98.—Read the Notes on P. 98.

***Experiment 28.**—*Detection of a Small Quantity of Arsenic.*—Add 2 drops of the test-solution of H_3AsO_4 to 10 cc. H_2SO_4, and treat the mixture by P. 99.—Read the Notes on P. 99.

Experiment 29.—*Analysis of Unknown Solutions for All the Basic Constituents.*—Ask the instructor for two unknown solutions for this purpose ("unknowns *G* and *H*"), and analyse 10 cc. of each of them by P. 11–95. Before precipitating with H_2S, exactly neutralize the solution with NH_4OH and add 5 cc. HNO_3.

> *Note.*—In complete analyses of this kind where a number of different precipitates and filtrates are successivly obtained, any of these that are set aside, even temporarily, should be distinctly labelled, in order to avoid mistakes. A convenient method of doing this is to mark on the label simply the Procedure by which the precipitate or filtrate is next to be treated; thus the H_2S precipitate would be marked P. 22, and the filtrate from it P. 51. The final tests for any element may be marked Test for Pb, Test for Al, etc.

DETECTION OF THE ACIDIC CONSTITUENTS.

Experiment 30.—*Detection of Carbonate and Nitrite.*—Test 5 drops of the test-solution of Na_2CO_3 (in place of "0.1 g. of the finely powdered substance") for carbonate by the first paragraph of P. 101. Test 5 drops of the test-solution of $NaNO_2$ for nitrite by the second paragraph of P. 101.—Read the General Discussion on pages 94–95, refer to Table XIII (page 97), and read the Notes on P. 101.

Experiment 31.—*Detection of Sulfate, Sulfite, and Fluoride.*—Mix together 2 cc. portions of the test-solutions of Na_2SO_4, Na_2SO_3, and HF, add 2 cc. HNO_3, and treat the mixture by P. 102. (Reject the $CaCl_2$ precipitate.)—Refer to Table XIV (page 98), and read the Notes on P. 102.

Experiment 32.—*Detection of Halides and of Chlorate.*—Mix together 2 cc. portions of the test-solutions of KCl and $KClO_3$, add 2 cc. HNO_3, and treat the mixture by P. 103.—Refer to Table XIV (page 98), and read the Notes on P. 103.

Experiment 33.—*Detection of Phosphate.*—To 2 cc. of the test-solution of Na_2HPO_4 add 2 cc. HNO_3, and treat the mixture by P. 104. —Read the Notes on P. 104.

Experiment 34.—*Detection of Thiocyanate.*—To 2 cc. of the test-solution of KSCN add 10 drops of HNO_3, and treat the mixture by P. 105.—Read the Notes on P. 105.

Experiment 35.—*Detection of the Separate Halides.*—Mix together 2 cc. portions of the test-solutions of KCl, KBr, and KI, and treat the mixture by P. 106.—Refer to Table XV (page 100), and read the Notes on P. 106.

Experiment 36.—*Analysis of an Unknown Solution for the Acidic Constituents tested for in Nitric-Acid Solution.*—Ask the instructor for an unknown solution for this purpose ("unknown *J*"). To 10 cc. of it add 15 cc. water and 5 cc. HNO_3, and treat portions of the mixture by P. 102–106.—Refer to Tables XIV and XV (pages 98 and 100).

***Experiment 37.**—*Distillation with Phosphoric Acid and Detection of Carbonate, Halides, and Sulfate.*—Mix 3 cc. portions of the test-solutions of Na_2CO_3, KCl, and K_2SO_4, and treat this mixture (in place of "2 g. of the finely powdered substance") by P. 111. Treat a portion of the second distillate by the first paragraph of P. 116. Treat the third distillate by P. 119.—Refer to Table XVI (page 104), and read the Notes on P. 111, 116, and 119.

***Experiment 38.**—*Detection of Sulfite.*—Add to 3 cc. of the test-solution of Na_2SO_3 10 cc. $Ba(OH)_2$ solution, acidify with HAc, and treat the mixture by the first paragraph of P. 112. Refer to the first part of Table XVII (page 107), and read the Notes on P. 112.

***Experiment 39.**—*Detection of Iodin-Liberating Constituents.*—Treat 10 cc. of the test-solution of NaOCl (which contains also an equivalent quantity of NaCl and some Na_2CO_3) by the first paragraph of P. 111. Treat the whole distillate so obtained by the first two paragraphs of P. 113.—Treat 3 cc. of the test-solution of KNO_2 by the first two paragraphs of P. 113.—Refer to the middle part of Table XVII (page 107), and read the Notes on P. 113.

***Experiment 40.**—*Detection of Cyanide.*—Treat 3 cc. of the test-solution of KCN by P. 115.—Refer to the last column of Table XVII (page 107), and read the Note on P. 115 and Notes 1–3, P. 107.

***Experiment 41.**—*Analysis of an Unknown Solution for Acidic Constituents passing into the Phosphoric Acid Distillates.*—Ask the instructor for an unknown solution for this purpose ("unknown *K*"), and treat 10 cc. of it by P. 111. Treat the distillates by P. 112–119. —Refer to Tables XVII and XVIII (pages 107 and 110).

Experiment 42.—*Detection of Borate.*—Treat 0.2–0.3 g. of solid borax ($Na_2B_4O_7$) by P. 121.—In connection with each one of Expts. 42–47 refer to Table XIX (page 112), and read the Notes on the Procedure involved in the Experiment.

Experiment 43.—*Detection of Fluoride.*—Treat 0.2–0.3 g. of solid CaF_2 by P. 122.

Experiment 44.—*Detection of Nitrate.*—Treat 0.2–0.3 g. of solid KNO_3 by P. 124.

***Experiment 45.**—*Detection of Nitrite.*—Treat 1 cc. of the test-solution of KNO_2 by P. 125.

***Experiment 46.**—*Detection of Hypochlorite.*—Treat 3 cc. of the test-solution of NaOCl by P. 126.

***Experiment 47.**—*Detection of Chlorate in Presence of Hypochlorite.* —Mix 3 cc. portions of the test-solutions of NaOCl and $KClO_3$, and treat the mixture by P. 127.

PREPARATION OF THE SOLUTION AND COMPLETE ANALYSIS OF UNKNOWN SOLID SUBSTANCES.

Experiment 48.—*Substances Soluble in Water or Dilute Acid.*—Ask the instructor for two such unknown substances ("unknowns I and II"), and treat portions of each of them by P. 1, by P. 2 followed by P. 11–95, by P. 96–98, and by P. 100, 101–107, 121, and 124–126.—Read the Notes on P. 1 and 2.—Record and report the results in the note-book as directed in the Note on Expt. 7. In the case of a solid substance not only report the constituents and the proportions of them present, but state the compound or compounds of which the substance seems to be mainly composed.

Note.—In analyzing unknown solids the quantity taken for the analysis should be weighed (within 0.1 g.) on a rough balance, not guessed at nor estimated by volume.

Experiment 49.—*Non-Metallic Substances requiring Treatment with Concentrated Acids.*—Ask the instructor for two such substances ("unknowns III and IV"), and treat portions of each of them by P. 1, by P. 2–3 (or 2–4, if necessary) followed by P. 11–95 (or 21–95), by P. 96–98, and by P. 100, 111–119, and 121–127. If there is any undissolved residue (of silica or silicate) at the end of P. 4, disregard it in these analyses.—Refer to Table I (page 29), and read Notes 1–4, P. 3, and Notes 1–2, P. 4.

Experiment 50.—*Alloys Dissolved by Concentrated Acids.*—Ask the instructor for two such alloys ("unknowns V and VI"), and treat 0.5 g. of each by P. 3–4 and P. 11–70 (or P. 21–70).—Read Notes 5–9, P. 3, and Notes 3–4, P. 4.

***Experiment 51.**—*Mineral Substances Not Completely Dissolved by Concentrated Nitric and Hydrochloric Acids.*—Ask the instructor for two such substances ("unknowns VII and VIII"). Treat 1 g. of each of them by P. 2–6, followed by P. 11–95.—Refer to Table I (page 29), and read the Notes on P. 5 and 6.—Treat fresh portions of each of the substances by P. 131.—Read the Notes on P. 131.

Ask the instructor for another such substance ("unknown IX"). Treat 1 g. of it by P. 2–4. Treat the solution obtained in P. 4 by P. 21–95, and the residue obtained in P. 4 by P. 7, followed by P. 21–89. Reserve, as directed, one-half of the aqueous extract of the fused mass obtained in P. 7, and test it for acidic constituents as described in the third and fourth paragraphs of P. 131.—Read the Notes on P. 7.—Treat fresh portions of the substance by P. 101 and P. 102–104.

***Experiment 52.**—*Substances Containing Organic Matter.*—Ask the instructor for such a substance ("unknown X"), and treat portions of it by P. 1, by P. 8 followed by P. 11–95, by P. 96–98, and by P. 101–106.—Read the Notes on P. 8.

QUESTIONS ON THE EXPERIMENTS.

DETECTION OF THE BASIC CONSTITUENTS.

Experiment 1.—1. In precipitating the silver-group in an actual analysis could the NH_4Cl be replaced by NaCl? by HCl? (*In the case of all questions which can be answered by "yes" or "no," giv the reasons for the answer.*)

2. If the NH_4Cl were not added, what would happen to the silver in the subsequent parts of the experiment?

3. Of the five basic constituents present in the mixture why is silver the only one that is precipitated by NH_4Cl?

4. If enough H_2S were not used to precipitate all the copper, how would it behave on the subsequent addition of NH_4OH and $(NH_4)_2S$?

5. What is the first reaction that takes place when NH_4OH is added to the filtrate from the H_2S precipitate?

6. What would happen to the $(NH_4)_2S$ if it were added directly to the filtrate from the H_2S precipitate, without first adding NH_4OH?

7. What happens to the $(NH_4)_2S$ when the filtrate from the $(NH_4)_2S$ precipitate is evaporated?

8. If all the basic constituents had been present in the original mixture used for this experiment, what ones would have been precipitated by (*a*) NH_4Cl, (*b*) H_2S, (*c*) NH_4OH and $(NH_4)_2S$, (*d*) $(NH_4)_2CO_3$? (*e*) What ones would have been left with the potassium in the filtrate from the $(NH_4)_2CO_3$ precipitate?

Experiment 2.—1. What would be meant by the statement that a certain quantity of lead nitrate is equivalent to a certain other quantity of ammonium chloride?

2. In making up one liter of a 1-normal solution of NH_4Cl, how many grams of the salt should be weighed out, and how much water should be added to it? (For the atomic-weight values needed in answering this and other questions see the table on page 124.)

3. In making up a liter of a 6-normal solution of H_2SO_4, how many cubic centimeters of 96% sulfuric acid (s. g., 1.84) should be used, and how much water should be added to it?

4. Approximately how many cubic centimeters of the NH_4Cl solution would be required to precipitate 500 mg. of silver? (Calculate first the number of equivalents corresponding to 500 mg. Ag.—Since 1 g. of the unknown substance is ordinarily taken for the analysis for basic constituents, 500 mg. is as large a quantity of any element as is likely to be present.)

5. Why is a considerable excess of NH_4Cl added? (The word *excess* signifies the quantity added beyond the equivalent quantity theoretically required to produce the reaction in question.)

6. The solubility of $PbCl_2$ at 20° in water is 0.070 equivalents per liter and in 0.2-normal NH_4Cl solution is 0.018 equivalents per liter. Explain by the solubility-product principle why NH_4Cl diminishes the solubility. (This question may be answered by shortening the complete explanation given in Note 6, P. 11, as follows: "In any dilute sol'n satur. with $PbCl_2$, $(Pb^{++})\times(Cl^-)^2 =$ satur. value. NH_4Cl added to such a sol'n causes, owing to its ionization into NH_4^+ and Cl^-, an increase in (Cl^-), and therefore raises $(Pb^{++})\times(Cl^-)^2$ above the saturation value, so that

$PbCl_2$ ppts." *(All other questions as to the effect of one substance on the solubility of another substance should be answered in a similar way. Always consider the effect which the added substance may have on the concentration of each of the ions of the salt with which the solution is saturated, and state the reason for any such effect.)*

7. Calculate by the solubility-product principle, from the fact that the solubility of $PbCl_2$ in water at 20° is 0.070 normal, what its solubility would be in a solution 0.16 normal in chloride-ion (which is approximately the chloride-ion concentration in a 0.2 normal NH_4Cl solution). Assume the $PbCl_2$ to be completely ionised.

8. From the data given in Question 6 calculate how many milligrams of lead would have to be present in 40 cc. water at 20°, in order that any precipitation of $PbCl_2$ may result on adding to it 10 cc. 1–normal NH_4Cl solution.

9. In the precipitation of bismuth by the NH_4Cl solution, what ion-concentration product comes into consideration? What must be true of its value in order that bismuth may be precipitated? Explain why increasing the HNO_3-concentration increases the quantity of bismuth that remains in solution.

10. The solubility of AgCl at 100° is 0.022 g. per liter. Calculate how many milligrams of silver might be lost if the chloride precipitate were washed with 100 cc. boiling water.

11. In testing for lead in P. 13, explain why the addition of an excess of H_2SO_4 to the solution diminishes the solubility of the precipitate, and thus increases the delicacy of the test.

12. What other elements besides lead might be precipitated by adding H_2SO_4 to a solution in which they were present? Since these other elements are precipitable by H_2SO_4, why does the formation of a precipitate in P. 13 show the presence of lead?

13. Explain by the solubility-product principle why the formation of the complex salt $Ag(NH_3)_2{}^+Cl^-$ causes AgCl to be much more soluble in NH_4OH solution than in water. (Answer in accordance with the Note on Question 6.)

14. Formulate the mass-action expression for the equilibrium between the complex cation $Ag(NH_3)_2{}^+$ and its constituents. Show by reference to this expression and the solubility-product principle why the addition of HNO_3 causes AgCl to be precipitated out of its solution in NH_4OH.

Experiments 3 and 4.—1. In precipitating with H_2S in P. 21 what is the reason for adding 5 cc. HNO_3 and diluting the solution to 100 cc.? Why not use less acid and thus avoid all risk of failing to precipitate the elements of the copper and tin groups?

2. In passing H_2S into a $Cu(NO_3)_2$ solution, at what stage in the process does the solution after shaking begin to smell of the gas?

3. What principle determins how the quantity of H_2S dissolved by a given quantity of water varies with its partial pressure? What would its partial pressure be in a mixture made by mixing 1 volume of H_2S with 4 volumes of air, each at a pressure of one atmosphere?

4. Why would a larger quantity of an element have to be present in order to giv a precipitate if in P. 21 the solution were treated with H_2S in an open beaker, instead of in the closed flask?

5. Giv two reasons why a larger quantity of an element would have to be present to giv a precipitate if the solution were saturated with H_2S at 80°, instead of at 20°.

6. The solubility (in equivalents per liter) of freshly precipitated ZnS in water is about 100 times as great as that of CdS. Calculate by the principles discussed in Note 4, P. 21, the ratio of the hydrogen-ion concentrations at which the precip-

itation of cadmium and zinc will barely take place when the concentration of each of them has any definit value (for example, 0.0001 equivalents per liter).

7. The pressure-volume relations of perfect gases are expressed by the equation $pv / T = 82 N$, when the pressure p is in atmospheres, the volume v in cubic centimeters, and the temperature T in centigrade-degrees on the absolute scale, and when the quantity of the gas is N gram-molecular-weights. Calculate the number of cubic centimeters of H_2S at 25° required to precipitate 500 mg. of copper.

8. By what reaction is the HNO_3 destroyed when the arsenic solution to which HCl has been added is evaporated to dryness? Could HCl be destroyed in the same way by evaporating a solution of chloride with HNO_3?

9. If the HNO_3 were not so destroyed, what would happen when the H_2S is passed into the hot, strongly acid solution?

Experiment 5.—1. What substances besides ferric salts might be present which would cause precipitation of sulfur in P. 21?

2. Write the equation expressing the reaction between each of these substances and H_2S, balancing the equations by the method described in Note 7, P. 21.

3. Write by the same method the equations expressing the oxidation of H_2S, in one case to sulfur and in another to H_2SO_4, by hot fairly concentrated HNO_3, assuming that the HNO_3 is reduced to NO.

Experiment 6.—1. Make a table showing briefly in the first column the chemical operations involved in analyzing a solution for mercury and lead (by P. 21 and P. 31–34), and showing in a second and in a third column the behavior of these two elements in each operation.—"Behavior" in this and later questions means both the effect observed and the chemical compound produced. Thus, the first two operations and the results of them should be entered as follows:

Operation	*Behavior of Mercury*	*Behavior of Lead*
Satur. with H_2S.	Black ppt. of HgS.	Black ppt. of PbS.
Boil with 2-n. HNO_3.	No change.	Ppt. diss., forming colorless sol'n of $Pb^{++}(NO_3^-)_2$.

2. Make a similar table showing the operations involved in analyzing a solution for bismuth, copper, and cadmium (by P. 21, 31, 33, and 35–38), and showing the behavior of these elements.

3. Explain by the solubility-product principle the fact that CuS, which is only slightly soluble in hot dilute HCl, dissolves readily in hot dilute HNO_3 of the same concentration.

4. Write the equation expressing the dissolving of CuS in the HNO_3.

5. Why is a black residue left undissolved by HNO_3 not sufficient evidence of the presence of mercury?

6. Suggest a reason why in the confirmatory test for mercury the addition of HCl with the $SnCl_2$ tends to prevent the immediate reduction of the Hg_2Cl_2 to Hg.

7. Why does the evaporation with H_2SO_4 convert the salts present into sulfates? Could sulfates be converted into nitrates by evaporating with a large excess of HNO_3?

8. Explain with reference to the solubility-product principle why $PbSO_4$ is much more soluble in dilute HNO_3 than in water. (H_2SO_4 in dilute solution is dissociated almost completely into H^+ and HSO_4^-; but the latter ion is only to a moderate extent dissociated into H^+ and $SO_4^=$).

9. What effect, as compared with that of HNO_3, would HCl have on the solubility of $PbSO_4$? What effect would KNO_3 have? Giv reasons. (K_2SO_4 in dilute solu-

tion, like other unibivalent salts, but unlike H_2SO_4, is almost completely dissociated into the simple ions, K^+ and $SO_4^=$, with formation of only a small proportion of the intermediate ion, KSO_4^-.)

10. Explain by the solubility-product principle why the fact that $PbAc_2$ is a slightly ionized substance should cause $PbSO_4$ to dissolve much more readily in NH_4Ac solution than in water.

11. Would you expect $PbCrO_4$ also to be more soluble in NH_4Ac solution than in water? Why or why not? if so, why does $PbCrO_4$ precipitate from the same NH_4Ac solution that dissolves $PbSO_4$?

12. Arrange all the compounds of lead thus far met with in the order in which their solubility in water decreases.

13. If in an actual analysis a precipitate of BiOCl formed on diluting the solution before passing in H_2S in P. 21 and that precipitate were filtered off, would a bismuth precipitate be obtained with NH_4OH in P. 35? if the BiOCl were not filtered off, would any change occur in it on passing in H_2S?

14. Explain with the aid of the mass-action expressions involved why $Cu(OH)_2$, a substance very slightly soluble in water, is not precipitated by the NH_4OH. Show that the presence of the $(NH_4)_2SO_4$ in the solution must diminish the tendency of it to precipitate.

15. If the lead were not removed by the addition of H_2SO_4, would it be precipitated as $Pb(OH)_2$ on the addition of NH_4OH? What knowledge in regard to lead compounds would enable one to predict whether or not this precipitation would take place?

16. Write the equations expressing the formation of Na_2SnO_2 from $SnCl_2$ and NaOH; also that expressing the spontaneous decomposition of Na_2SnO_2 into tin and Na_2SnO_3; also that expressing its action on BiO_3H_3.

17. Lead hydroxide, like $Sn(OH)_2$, is an amphoteric substance. What is meant by this statement? What experiments might be made to determin whether it is true?

18. If $K_4Fe(CN)_6$ be added in P. 37 to the ammoniacal solution (without neutralizing it with HAc), no precipitate is produced unless a fairly large quantity of copper is present. Explain this fact.

19. Show from the solubility-product expressions that, if $Cd_2Fe(CN)_6$ is much more soluble than $Cu_2Fe(CN)_6$, the former can not be precipitated till enough $K_4Fe(CN)_6$ has been added to precipitate practically all the copper.

20. What change is observed which shows that the complex copper-ammonia ion is completely decomposed when KCN is added to the solution?

21. CdS is much more soluble in water than Cu_2S. Why is CdS precipitated by H_2S from the KCN solution, while Cu_2S is not?

22. In dissolving the sulfides in P. 31, if a HNO_3 solution stronger than 2-normal were used, or if the solution were boiled too long, and in consequence some mercury dissolved, how would it behave in the subsequent Procedures?

23. If in evaporating the HNO_3 solution with H_2SO_4 in P. 33 the evaporation were stopped before all the HNO_3 was expelled, what effect would this error have on the tests for lead, bismuth, and cadmium?

Experiments 8–9.—1. Write chemical equations expressing the two stages of the hydrolysis of $(NH_4)_2S$. Explain by the ionic theory and the mass-action law why this hydrolysis takes place, taking into account the fact that water is ionised to a slight extent into H^+ and OH^-.

2. Write the equations expressing the action of HCl on a solution of ammonium monosulfide, and on one of ammonium polysulfide (regarding the latter as $(NH_4)_2S_2$).

3. Write equations expressing the behavior of a solution of $AsCl_3$ when treated in succession with H_2S in P. 21, with ammonium polysulfide in P. 22, and with HCl in P. 23.

4. Explain by the solubility-product principle why the addition of HCl to a solution of $(NH_4)_2SnS_3$ causes the precipitation of SnS_2.

5. Make a table showing the solubility of each of the sulfides of the copper and tin groups in both ammonium monosulfide and ammonium polysulfide. Indicate in each case whether the sulfide is readily soluble, slightly soluble, or practically insoluble.

6. Why does not Bi_2S_3 dissolve in $(NH_4)_2S$, just as Sb_2S_3 does? Why does not SnS dissolve in ammonium monosulfide as well as in ammonium polysulfide?

7. Why not use in all cases ammonium polysulfide, since this readily dissolves all the tin-group sulfides? Why is the precipitate first treated with a small quantity of it, even tho this makes necessary a second treatment?

8. Why does the tendency of copper to form the complex copper-ammonia ion not cause CuS to dissolve in NH_4OH? What must be the explanation of the fact that some CuS dissolves in ammonium polysulfide?

Experiment 10.—1. Describe specifically the differences in the behavior of the sulfides of arsenic, antimony, and tin on which the separation of these three elements is based.

2. In treating the sulfides with 12-normal HCl why does much more As_2S_5 dissolve if the solution be allowed to boil? Why does it boil at so low a temperature as 50–60°?

3. Write by the method described in Note 7, P. 21, the equations expressing the action of HCl on $KClO_3$ by which Cl_2 is produced and that by which ClO_2 is produced.

4. Explain why the Cl_2 set free by the addition of the $KClO_3$ causes the As_2S_5 to dissolve even in the dilute HCl.

5. What is the expression for the solubility-product in the case of $MgNH_4AsO_4$? Why does it dissolve readily in HCl?

6. Why does the hydrolysis of this salt increase its solubility? Why is that hydrolysis decreased by an excess of NH_4OH? How is the hydrolysis affected by the presence of NH_4Cl? Would NH_4Cl affect the solubility in any other way?

7. What is a saturated solution? a supersaturated one? By what treatments can a precipitate be made to separate from a supersaturated solution?

8. What difference in the ionization causes the behavior of arsenic acid towards H_2S to be different from that of other elements of the copper and tin groups? What causes its own behavior to be different in dilute and concentrated HCl solutions?

9. Write the series of reactions which take place when H_2S is passed into a dilute HCl solution of H_3AsO_4. State what is known about the rate or equilibrium of each of these reactions.

10. Explain why antimony precipitates on the platinum rather than on the tin, and state how would the result be different if the tin did not touch the platinum?

11. Why does the tin dissolve in HCl more readily when it is in contact with the platinum?

12. In the confirmatory test for tin, why is lead used instead of zinc?

13. If zinc were used, how would the procedure have to be modified?

14. In the confirmatory test for tin how does the precipitation of a mercury compound show the presence of tin?

15. If the antimony were not all precipitated in P. 44 on passing H_2S into the hot solution, how would it behave in the subsequent procedure (P. 46) in which the tin is precipitated and its presence confirmed?

Experiment 12.—1. In an actual analysis how many cubic centimeters of NH_4OH would be required to neutralize the 5 cc. HNO_3 that are added before precipitating with H_2S?

2. How much more NH_4OH would be needed to neutralize the solution if 500 mg. Cu had been present in the form of $Cu(NO_3)_2$ in the solution precipitated by H_2S? (In all such calculations of the volume of the reagent needed, first reduce the weight of the constituent from grams to equivalents.)

3. How does testing the vapors above the solution with $PbAc_2$-paper show that an excess of $(NH_4)_2S$, a non-volatil salt, has been added?

4. If in an actual analysis the mixture containing NH_4OH and $(NH_4)_2S$ were allowed to absorb CO_2 from the air before filtering, what difference would it make?

5. Why is the $(NH_4)_2S$ precipitate treated first with cold HCl? Why is HNO_3 subsequently added?

Experiments 13 and 14.—1. Which elements are soluble, *a*, in excess of NH_4OH (in the presence of NH_4Cl), but not in excess of NaOH; *b*, in excess of NaOH, but not of NH_4OH (in presence of NH_4Cl); *c*, in excess both of NH_4OH and of NaOH; *d*, neither in excess of NaOH nor of NH_4OH (in presence of NH_4Cl)?

2. What are the explanations of the four typical cases *a*, *b*, *c*, *d*, referred to in the preceding question?

3. Could the hydroxide of an element which does not form a complex ammonia cation be soluble in NH_4OH and not in NaOH? Could an amphoteric hydroxide be readily soluble in NaOH and entirely insoluble in NH_4OH?

4. Show by formulating and combining the two mass-action equations involved that the quantity of aluminum dissolved (as AlO_2^-) in the presence of a base is proportional to the OH^- concentration in the solution.

5. Name all the elements that form ammonia complexes in all the groups thus far considered. What can be said as to the position of these elements in the periodic system? (Refer to a text-book of Inorganic Chemistry.)

6. If in an actual analysis no precipitate is obtained on the addition of NH_4OH, what conclusion may be drawn?

7. Which of the hydroxides precipitated by NaOH undergo change on the addition of Na_2O_2, and into what compound is each of these hydroxides converted?

8. What substances are produced by the action of Na_2O_2 on water?

Experiment 15.—1. What does Expt. 15 show in regard to the behavior of the alkaline-earth elements in an actual analysis?

2. What must be the explanation of the fact that the phosphate combines with the iron rather than the calcium when both these elements are present?

3. If phosphate is known to be present, is it necessary to test for alkaline-earth elements in the filtrate from the $(NH_4)_2S$ precipitate?

4. If the original substance were soluble in water, would it be necessary to test for these elements in the $(NH_4)_2S$ precipitate?

5. If $CaCO_3$ were substituted for $Ca_3(PO_4)_2$ in the first part of Expt. 15, what would the result have been?

6. If a solution of $Ca_3(PO_4)_2$ in HCl were treated by the second paragraph of P. 52, what would happen on the addition of each reagent? What would happen, if a large proportion of $FeCl_3$ were also present in the phosphate solution?

Experiment 16.—1. Make a table (like that described in Question 1 on Expt. 6) showing the operations involved and the behavior of the chromium and zinc in analyzing a dilute HNO_3 solution of $ZnCrO_4$, beginning with the H_2S precipitation (P. 21) and continuing through the analysis of the aluminum-group (P. 51–57). At the foot of the table write all the chemical equations involved.

2. In separating the aluminum from the chromium and zinc with NH_4OH in P. 53, what would be the harm of adding too small an excess? what of adding too large an excess?

3. By what reagent other than $BaCl_2$ could the chromate be precipitated? What disadvantage would there be in the use of this reagent?

4. How can sulfate be present in the solution to which $BaCl_2$ is added?

5. How could a precipitate of ZnS be distinguished from one of sulfur by adding a suitable reagent to the liquid containing it?

6. What happens to nitrates, such as $Zn(NO_3)_2$ or $Co(NO_3)_2$, when they are ignited, as in the confirmatory test for zinc?

Experiment 17.—1. What are the oxides of manganese corresponding to its three stages of oxidation occurring in P. 61 and 62? What is the valence of manganese in each of these oxides? How do they differ with respect to the formation of salts with acids and with bases?

2. Make a table (like that described in Question 1 on Expt. 6) showing the operations involved and the behavior of manganese in analyzing a dilute HNO_3 solution of $CaMnO_4$, beginning with the H_2S precipitation and continuing through the final test for manganese (thus involving P. 21, 51, 52, 61, and 62). Write also all the chemical equations involved.

3. Why is a considerable excess of NH_4OH added in precipitating the iron in P. 64?

4. If FeS were treated by P. 31–38, how would it behave with each of the reagents?

5. Why is it necessary to test for zinc in the analysis of the iron-group?

6. Why may zinc be precipitated by NaOH and Na_2O_2 in the first treatment (in P. 52), and yet not be precipitated by them in the second treatment (in P. 67)?

7. When the original Na_2O_2 precipitate is so small that it need not be tested for zinc, how may P. 67–68 be simplified?

8. When the H_2S precipitate obtained in P. 66 is small, how may P. 67–68 be simplified?

Experiment 18.—1. If the H_2S and Na_2O_2 precipitates were not washed free from ammonium and sodium salts before dissolving them in P. 68, what might happen upon the addition of the HCl-ether reagent?

2. Suggest an explanation of the fact that, tho $NiCl_2$ is precipitated as a yellow compound by the HCl-ether reagent, it has a green color even in very concentrated aqueous solution.

3. Suggest any possible differences in the molecular state of $CoCl_2$, which might account for the facts that it has a pink color, like that of $Co(NO_3)_2$, in a dilute aqueous solution, and a blue color in an ether solution or a concentrated aqueous solution saturated with HCl.

4. Name all the elements thus far considered which in any state of oxidation form colored compounds in solution. What can be said as to the position of these elements in the periodic system?

5. Write equations expressing the steps in the chemical process by which the precipitate of potassium cobaltinitrite may be considered to be formed.

6. Does the NO_2^- coming from the excess of KNO_2 diminish the solubility of the precipitate in the same way as the K^+ does? What else, from a mass-action standpoint, might it be expected to do?

Experiment 19.—1. Why must the HNO_3 be removed before testing for iron with KSCN?

2. Make a table showing the operations involved and the behavior of $Ca_3(PO_4)_2$ in analyzing a HNO_3 solution of it by P. 51–52, P. 61, and P. 65.

3. Why does the NH_4Ac solution become red only when the quantity of iron is more than equivalent to the quantity of phosphate present?

4. What is meant by a basic salt? What are two possible simple formulas for basic ferric acetate?

Experiment 21.—1. What does this experiment show as to the precipitation by $(NH_4)_2CO_3$ of magnesium and of the other alkaline-earth elements (which all behave nearly as calcium does)?

2. Why would a reagent which consisted of NH_4HCO_3 not be suitable for the precipitation?

3. Why is there any advantage in adding more NH_3 than corresponds to the neutral salt $(NH_4)_2CO_3$?

4. If it were desired to work out a procedure for separating calcium, barium, and strontium from magnesium by means of $(NH_4)_2CO_3$, what experiments would one naturally make?

Experiment 22.—1. In order to make a separation of 1 mg. barium from 500 mg. strontium, what must be the concentration of $CrO_4^=$, stated with reference to the saturation-values of the ion-concentration products of $BaCrO_4$ and $SrCrO_4$?

2. What must be true of the relativ values of these two saturation-values in order that this separation may be possible? What is the actual ratio of these two values? (See the Table of Solubilities on page 124.)

3. Write the chemical equations for the conversion of chromate-iron into hydrochromate-ion, and for the conversion of the latter into bichromate-ion. Write also the mass-action expressions for the equilibrium of these reactions. Show by them what determins the proportion of $CrO_4^=$ and of $HCrO_4^-$ in any solution, and what determins the concentration of $Cr_2O_7^=$ in any solution.

4. In practis what three substances must be added in proper proportions in order to secure the right $CrO_4^=$ concentration in the solution?

5. Why is the second K_2CrO_4 precipitate obtained in the confirmatory test for barium more conclusiv evidence of its presence than the first K_2CrO_4 precipitate?

6. On addition of NH_4OH in P. 84 what chemical change causes the change in color from orange to yellow? Why from a mass-action standpoint does the addition of NH_4OH cause this change to take place? Why does this change cause strontium to precipitate?

7. Explain fully with reference to the saturation-values of the ion-concentration products why the carbonate-chromate mixture used in P. 85 does not affect $BaCrO_4$, and why it converts $SrCrO_4$ into $SrCO_3$.

8. Why does CaC_2O_4 dissolve in dilute H_2SO_4, but not in HAc?

9. How does the confirmatory test for calcium distinguish it from barium and strontium, which form much less soluble sulfates? How does it distinguish calcium from magnesium?

10. Could magnesium be precipitated by any other reagent in the form of a compound closely analogous to magnesium ammonium phosphate?

11. Why is the production of a precipitate with Na_2HPO_4 in the confirmatory test for magnesium (in P. 89) more conclusiv evidence of its presence than the production of the first Na_2HPO_4 precipitate (in P. 88)?

Experiment 23.—1. If the ammonium salt were not completely removed by the ignition, how would it behave in the subsequent tests for potassium?

2. Why is the separation of potassium and sodium by the $HClO_4$ method satisfactory when these elements are present as chlorides or nitrates, but not when they are present as sulfates? Why is it satisfactory when they are present as phosphates?

3. What is implied by the statement that $Na_3Co(NO_2)_6$ is a complex salt in solution?

4. How might a solution of $Na_3Co(NO_2)_6$ be prepared, judging from previous experience with an analogous compound?

Experiments 26 and 27.—1. Describe in detail the method by which it can be shown that the magnetic oxide of iron (Fe_3O_4) contains both ferrous and ferric iron.

2. Describe a method by which it can be shown that a solution contains both mercurous and mercuric salts.

3. What indications of the state of oxidation of tin would be afforded by the treatment with H_2S in P. 21, and with $(NH_4)_2S$ in P. 22, of a solution of $SnCl_2$? of solution of $SnCl_4$?

4. What other constituents besides iron, mercury, and tin exist in two stages of oxidation in the form of salts? Giv the symbols of compounds illustrating these two states of oxidation.

5. Mention any phenomena that might be observed during the course of analysis which would distinguish from each other the two stages of oxidation of each of the constituents named in the answer to Question 4.

Experiments 28 and 29.—1. What indication of the state of oxidation of arsenic may be obtained in the course of the analysis for the basic constituents?

2. What do the facts that concentrated HCl converts much H_3AsO_3, but very little H_3AsO_4, into the corresponding chloride show as to the ionization of these two substances?

3. What reaction occurs when the $CuSO_4$ solution is poured into the hydrogen generator in P. 99? How does the addition of the $CuSO_4$ accelerate the evolution of hydrogen?

DETECTION OF THE ACIDIC CONSTITUENTS.

Experiment 31.—1. With the aid of the laboratory experience and the statement as to solubilities on page 31 arrange the barium salts of the acidic constituents listed on page 94 in four groups comprising respectivly: those readily soluble in water; those only slightly soluble in water, but readily soluble in HAc; those only slightly soluble in HAc, but readily soluble in dilute HCl; and those only slightly soluble in dilute HCl.

2. Explain the following facts with reference to the ionization-values given in the Table on page 123: *a*, a precipitate of $Ba_3(PO_4)_2$ is converted into one of $BaHPO_4$ by a nearly equivalent quantity of HAc; *b*, $BaHPO_4$ is readily soluble in an excess of HAc with formation of $Ba(H_2PO_4)_2$ and $BaAc_2$; *c*, $BaHPO_4$ is readily soluble in dilute HCl with formation of H_3PO_4 and $BaCl_2$; *d*, $BaSO_3$ is not much more soluble in HAc than in water, but is readily soluble in dilute HCl; *e*, $BaCrO_4$ is not readily soluble in HAc, even tho $HCrO_4^-$ is very slightly ionized.

3. State how fluoride when present in large quantity behaves in each step of P. 102; and explain this behavior with reference to the ionization of HF and the solubility-values given in the table on page 124.

4. What other acidic constituent besides fluoride is shown by the solubility-table on page 124 to form a calcium salt less soluble than the barium salt? Show by reference to the solubility and ionization values involved how this constituent (in comparison with fluoride) might be expected to behave in each step of P. 102.

5. Suggest a reason why chromate, tho included in P. 102, is not added to the mixture (of Na_2SO_4, Na_2SO_3, and KF) used in Expt. 31 in illustrating that Procedure.

Experiment 32.—1. What disadvantage would there be in substituting $Pb(NO_3)_2$ for $Cd(NO_3)_2$ in the test for sulfide in P. 103?

2. Arrange the silver salts of the acidic constituents listed on page 94 in three groups comprising respectivly: those readily soluble in water; those only slightly soluble in water, but readily soluble in dilute HNO_3; and those only slightly soluble in dilute HNO_3.

3. Explain by reference to the solubilities of the salts (as given in the Table on page 124) and the ionizations of the corresponding acids why each of the salts in the second group referred to in the previous question dissolves in dilute HNO_3.

4. Explain why the silver halides do not dissolve in dilute HNO_3.

5. Explain why Ag_2S is only slightly soluble in dilute HNO_3, even tho the ionization of HS^- is extremely small.

6. Explain why $Ag_2(CN)_2$ is only slightly soluble in dilute HNO_3, even tho HCN is only very slightly ionized.

7. Why would it not be satisfactory to precipitate (and thus partially identify by their color) the silver salts which are soluble in dilute HNO_3, but not in water, by adding to the filtrate from the silver halides an excess of NaOH? Why not by adding an excess of NH_4OH?

Experiment 35.—1. State the principles involved in the process used for the detection of the three halides in the presence of each other.

2. Does the fact that only a very small quantity of bromin is liberated in the first step of the process mean that the reaction between the bromide and $KMnO_4$ is in equilibrium under the conditions prevailing in the solution?

3. What is meant by the statement that a reaction is in equilibrium? How would one proceed to determin whether a given reaction-mixture is in equilibrium?

4. If the mixture of KBr, NaAc, HAc, and $KMnO_4$ were allowed to stand a day or a week, what would happen?

5. Why must the iodin set free in the first part of the process be completely extracted by the chloroform?

6. Why is H_2SO_3 added in the last part of the process? Write the equation for the reaction which it causes.

7. Why is HNO_3 added with the $AgNO_3$ at the end of the process?

Experiment 37.—1. What two things determin whether or not an acid passes over into the first distillate?

2. Show by reference to the mass-action expressions for the ionization of the two acids what determins the extent to which an acid is displaced from its salt by another acid, taking K^+CN^- and $H^+H_2PO_4^-$ as an example.

3. Explain by reference to the ionization-values involved why $BaCO_3$ dissolves on adding HAc, and why $BaSO_3$ does not.

4. Show how phosphoric, pyrophosphoric, and metaphosphoric acids are related to one another in composition.

5. If a compound of an element forming an insoluble phosphate (for example, $CaCO_3$) were distilled with H_3PO_4, would the insoluble phosphate separate in the distilling flask? Explain why or why not.

6. If H_2SO_3 is found in the first distillate, which of the other substances that may be in that distillate is it unnecessary to test for? Write the equation for the reaction which would take place between H_2SO_3 and each of these substances.

7. If any of the H_3PO_4 were thrown over mechanically into the first distillate, what erroneous conclusion might be drawn in connection with P. 111?

Experiment 38.—1. What different constituents of the original substance may giv rise to sulfur in the distillate? what ones to sulfurous acid?

2. Show that H_3PO_4 which had been thrown over mechanically into the first distillate would not interfere with the tests for sulfite in P. 112.

Experiment 39.—1. What different constituents in the original substance may giv rise to chlorin in the first distillate? Write chemical equations illustrating its production from each of these constituents.

2. What different substances that might be present in the distillate would cause iodin to be set free on the addition of KI?

3. What conclusions could be drawn from the tests of the first two paragraphs of P. 113 as to the presence or absence of each of the three halogens in a distillate containing the following halogens: *a*, I_2, Br_2, and Cl_2; *b*, Br_2; *c*, Cl_2; *d*, no halogen?

4. Explain the fact that iodin is extracted by chloroform more slowly from an aqueous solution when it contains iodide. State the law that determins the quantity extracted.

5. Write chemical equations illustrating the process by which a small quantity of HNO_2 liberates a large quantity of iodin from KI.

Experiment 40.—1. Write the chemical equations involved in the test for cyanide.

2. Into what compounds is $K_4Fe(CN)_6$ decomposed when it is distilled with H_3PO_4?

3. Referring to the results of Expt. 26 with ferrous and ferric salts, suggest how a ferrocyanide could be distinguished from a ferricyanide by tests applied to a solution of the original substance.

Experiment 41.—1. To what extent is the analysis of the second distillate simplified when $AgNO_3$ givs no precipitate?

2. Some H_3PO_4 may pass over into the second distillate. Would Ag_3PO_4, which is only slightly soluble in water, precipitate in the $AgNO_3$ test, and thus obscure the test for the other constituents?

3. When is it necessary to test the second distillate for sulfide?

4. Explain by the mass-action principles why a sulfide may giv off an appreciable quantity of H_2S only in the second part of the distillation.

5. What constituents in the substance are likely to giv rise to chlorin in the second distillate? to bromin? to iodin?

Experiment 42.—1. Why not test for boric acid in the distillates obtained in the H_3PO_4 distillation?

2. What is the advantage in P. 121 of distilling the borate with H_2SO_4 and CH_3OH, rather than with H_2SO_4 with water?

Experiment 43.—1. Why must all the substances used in the test for fluoride be thoroly dry?

2. What happens to $KHSO_4$ when it is heated?

3. What are the main constituents of glass? What is the action of HF on it?

4. Since H_2SiO_3 is non-volatil, how can the deposit be driven up the tube by heating?

5. Of what does the white deposit left after washing the tube with water consist?

6. Show why it is appropriate to call the compound H_2SiF_6 "fluo-silicic" acid.

7. Why is it not satisfactory to test for fluoride in the distillates obtained in the H_3PO_4 distillation?

Experiments 44 and 45.—1. If chlorate were present in the substance, what would happen to it when treated by P. 124?

2. Iodin is not completely reduced to HI by $FeSO_4$, the four substances I_2, HI, ferrous salt, and ferric salt all being present in considerable quantity at equilibrium. If a solution containing ferric sulfate and KI were submitted to P. 124, what would be the result?

3. How might the distillation-process of P. 124 be modified so as to detect in two steps, first, the presence of nitrite, and second, when it is absent, the presence of nitrate?

Experiment 46.—1. What different substances are present in the solution produced by acidifying the NaOCl solution with HAc?

2. What advantage would there be in making the hypochlorite test in alkaline solution, rather than in HAc solution? What disadvantage?

3. Assuming that the oxidation of the $PbAc_2$ to PbO_2 is caused by HOCl, but not by Cl_2, explain why the oxidation does not take place in a solution strongly acidified with HNO_3.

Experiment 47.—1. How may a chlorate giv off chlorin in the first part of the H_3PO_4 distillation? How in the second part?

2. Write the equation expressing the reaction that takes place between NaOCl and $NaAsO_2$.

3. If the hypochlorite were not reduced, AgCl and $AgClO_3$ would be formed in the HNO_3 solution by the action of the Cl_2 on the $AgNO_3$. Write the equation expressing this reaction.

PREPARATION OF THE SOLUTION.

Experiment 48.—1. Of what elements is organic matter mainly composed, and what causes it to blacken on heating?

2. Describe a method by which a substance might be tested for organic matter by converting the carbon into carbon dioxide.

3. Could a sirup be tested for aluminum by diluting it with water and analysing the solution in the usual way? Could it be so tested for iron?

4. Name the different forms in which water may be present in a substance.

5. If a substance were ignited at a red heat (for example, to destroy organic matter) before submitting it to analysis, what basic constituents would be lost?

6. State how each of the following substances would behave in the closed-tube test: *a*, Na_3AsO_4; *b*, $MgNH_4PO_4$; *c*, FeS_2; *d*, $Pb(NO_3)_2$; *e*, $NaC_2H_3O_2$.

7. What acidic constituents will be detected, when present in considerable quantity, upon treating the substance with dilute HNO_3?

8. What is the behavior towards litmus of an aqueous solution of each of the following substances: Na_2SO_4; Na_2CO_3; $NaHCO_3$; $NaHSO_4$; $Ca(NO_3)_2$; $Fe(NO_3)_3$?

9. Name the basic constituents whose salts are nearly all readily soluble in water.

10. Name the basic constituents whose salts are decomposed by water, but dissolved by dilute acids.

11. Name the acidic constituents whose salts are all or nearly all readily soluble in water.

12. Name the acidic constituents whose salts (except those of the alkali elements) are nearly all very slightly soluble in water.

13. Of the groups of salts named in the answer to Question 12, which are readily soluble in cold dilute HNO_3 or HCl? Why?

14. In a substance soluble in water which has been found to contain barium, which of the following constituents would it be unnecessary to test for: nitrate, phosphate, sulfide, sulfite, chloride, sulfate, carbonate?

Experiments 49 and 50.—1. What group of salts not dissolved by cold dilute HNO_3 are decomposed by hot concentrated HNO_3, because of its oxidizing action?

2. State what happens (that is, what chemical changes occur and what phenomena are observed) at each step of the process when $PbSiO_3$ (which is decomposed by strong acids) is treated by P. 3.

3. State what happens at each step, namely, on heating with strong HNO_3, on evaporating to dryness and adding cold dilute HNO_3, and on heating the residue with strong HCl, when each of the following substances is treated by P. 3 and 4: *a*, Sb_2S_3; *b*, MnO_2; *c*, $PbSO_4$.

4. What metallic elements are scarcely ever found in alloys? How may the process of analysis therefore be shortened?

5. If there is no residue after treating an alloy by P. 3, what does it show as to the absence of certain elements?

Experiment 51.—1. State what happens to each of the substances whose symbols are given under *b* in Table I on fusing it with Na_2CO_3, on treating the fused mass with water, and on treating the residue with dilute HNO_3, as described in P. 7.

2. What are the only acidic constituents that it is ordinarily necessary to test for in minerals?

3. State what happens to each of the substances whose symbols are given under *b* in Table I when it is treated, as in P. 5: (1) with concentrated H_2SO_4; (2) then with HF; (3) then, after evaporating to fuming, with water.

4. State what happens to feldspar (potassium aluminum silicate, an example of a silicate not much decomposed by acids other than HF) when it is treated by P. 5.

5. Explain with reference to the solubilities of the substances involved why $PbSO_4$ is completely converted into $PbCO_3$ by boiling with Na_2CO_3 solution in P. 6; and why $BaSO_4$, when much of it is present, is only partly converted into $BaCO_3$ by the same treatment.

PART II.

THE SYSTEM OF ANALYSIS.

PREPARATION OF THE SOLUTION.

PRELIMINARY EXAMINATION.

Procedure 1.—*Preliminary Examination.*—If the substance is a non-metallic solid, note its color, odor, and texture; examin it with a lens to determin whether it is heterogeneous, and, if so, note the appearance of its constituents. To determin whether organic matter or water is present and to get other indications, heat gently at first, then strongly, about 0.1 g. (0.1 gram) of the finely powdered substance in a hard glass tube (of about 0.6 cm. bore and 10 cm. length) closed at one end. Note whether the substance blackens, whether a tarry, aqueous, or other deposit forms on the cold part of the tube, and whether any odor is emitted. If organic matter is thus proved to be absent, pass to P. 2 (Procedure 2); if proved to be present, to P. 8.

If the substance is an alloy, treat it by P. 3.

If the substance is a solution, evaporate a measured volume of it to dryness in a small weighed dish, dry the residue thoroly at 120–130° in a hot closet or by keeping the dish in motion over a small flame, and weigh the dish again. Heat a portion of this residue in a closed tube as described above. Treat another portion by P. 2 if organic matter is absent, or by P. 8 if organic matter is present.

Notes.—1. When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter is present; for certain kinds of organic matter, especially sugars and hydroxy-acids, such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of most of the elements by alkalies. Such organic matter must therefore be detected and removed in order to ensure the precipitation of aluminum and chromium by NH_4OH. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. Alloys do not contain organic matter or water; and therefore the closed-tube test need not be applied to them.

2. Blackening accompanied by a burnt odor or by the formation of a tarry deposit shows organic matter. Blackening alone does not show it; for copper, cobalt, and nickel salts may turn black on heating, owing to the formation of the black oxides.

3. It is usually desirable to determin whether water is a constituent of the substance, and, if so, whether it is present in large or small proportion. This can be done with a fair degree of delicacy by the closed-tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. Water may be present as so-called water of constitution, as in FeO_3H_3 or Na_2HPO_4; as water of crystallization, as in $MgSO_4.7H_2O$; as enclosed water, as in some hydrated silicates like the zeolites or as mother-liquor within crystals; and as hygroscopic moisture on the surface. Water of constitution may be expelled only at a fairly high temperature, while in the other forms it is seldom retained above 200°.

4. The closed-tube test may also furnish evidence of the presence of certain basic and acidic constituents when they are present in considerable quantity. Thus all ammonium salts and mercury compounds are volatilized much below a red heat. Ammonium salts and the chlorides of mercury giv a white sublimate. Most other mercury compounds giv a gray one, consisting of minute globules of mercury, made visible by a lens or by rubbing with a wire. Metallic As, As_2O_3, and As_2S_3 are also readily volatilized, forming black, white, and yellow sublimates, respectivly. Of the acid-forming elements or groups, free sulfur or a persulfide is shown by a sublimate of reddish-brown drops, changing to a yellow solid on cooling, and accompanied by odor of SO_2; a moist sulfide, by the odor of H_2S; a nitrate or nitrite, by brown vapors of NO_2; free iodin or a decomposable iodide, by a black sublimate of I_2 and by its violet vapor; a sulfite, by the odor of SO_2; a peroxide, chlorate, or nitrate, by evolution of oxygen, recognized by its inflaming a glowing wood-splinter held in the tube; and a carbonate or oxalate, by the evolution of CO_2, recognized by its causing turbidity in a drop of $Ba(OH)_2$ solution.

5. If the substance to be analyzed is a liquid, it is desirable to determin by evaporation how much, if any, solid substance is present in it; for enough must be taken for analysis to enable small quantities of the basic constituents to be detected. Moreover, if it is dissolved in a volatil organic solvent the latter must be removed by evaporation.

PREPARATION OF THE SOLUTION.

TABLE I.—PREPARATION OF THE SOLUTION IN THE CASE OF NON-METALLIC SUBSTANCES.

<table>
<tr><td colspan="6">*Heat the substance with water and dilute HNO_3 (P. 2).*</td></tr>
<tr><td rowspan="4">*If it all dissolves, treat the solution by P. 11.*</td><td colspan="5">*If it does not all dissolve, add more HNO_3, evaporate, dry completely, add dilute HNO_3 (P. 3).*</td></tr>
<tr><td rowspan="3">Substances decomposed: many sulfides and silicates. *Treat the solution by P. 11.*</td><td colspan="4">Residue:* a. Sb_2O_5, H_2SnO_3, MnO_2, PbO_2, HgS, $PbCrO_4$, $BaCrO_4$. b. C, Al_2O_3, Cr_2O_3, AgCl, CaF_2, $PbSO_4$, $BaSO_4$, $SrSO_4$, SiO_2, and many silicates and fluosilicates.
Heat with HCl or HCl and HNO_3, evaporate, add dilute HCl (P. 4).</td></tr>
<tr><td rowspan="2">Solution: substances under a. *Treat by P. 21.*</td><td colspan="3">Residue: substances under b.
Heat with H_2SO_4 and HF, evaporate off the HF, add water, boil (P. 5).</td></tr>
<tr><td>Gas: SiF_4.</td><td>Residue: Pb, Ba, Sr,(Cr), as sulfates. *Treat by P. 6.*</td><td>Solution: other elements as sulfates. *Treat by P. 11.*</td></tr>
</table>

* Only the more common substances that are likely to be present in the residue are here mentioned.

Procedure 2.—*Treatment of Non-Metallic Substances Free from Organic Matter.*—Weigh out on a rough balance 1 g. of the finely powdered substance (see Note 1), add to it in a casserole 20 cc. water, heat the mixture to boiling if there is a residue, and test the solution with litmus paper. Add to the mixture 6–normal HNO_3, a few drops at a time, till after shaking it becomes distinctly acid. Note whether there is an odor or effervescence. Then add, without filtering out any residue and without further heating, just 5 cc. 6–normal HNO_3.

If the substance has dissolved completely, treat the solution by P. 11.

If the substance has not dissolved completely, treat the mixture, without filtering out the residue, by P. 3. (See Note 8.)

Notes.—1. In order that difficultly soluble substances may be dissolved, the substance must be reduced to a very fine powder. This is usually best accomplished by grinding the substance, a small quantity at a time, in a porcelain or agate mortar. With hard substances, and in general with minerals, an agate mortar should be used. As such a mortar is likely to be broken by a blow, the substance should be ground, not pounded, in it.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitativ analysis should not only show the presence or absence of the various elements in the substance, but should enable their relativ quantities to be estimated. Since 1 or 2 mg. of almost any element can be detected by this system of analysis, the presence of 0.1–0.2% of an element will be detected when one gram of substance is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them. Moreover, the directions given for some of the separations are based on the assumption that not more than 500 mg. of any one constituent is present.

3. When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyze it and the solution separately, unless special information in regard to the soluble constituents is desired. It is, therefore, directed to treat at once with HNO_3. The mixture is not heated after addition of the acid, so as to avoid oxidizing mercurous, arsenous, and ferrous salts. Only 20 cc. of water are used so that the acid may be strong enough to prevent the hydrolysis of salts of bismuth and tin, and thus ensure their solution.

4. Just 5 cc. 6–normal HNO_3 must be present in order that the acid concentration may be properly adjusted in the subsequent H_2S precipitation. For this reason, when the solution is alkaline or when a substance (like an undissolved oxide or carbonate) which neutralizes the acid is present, the solution is made distinctly acid before adding the 5 cc. of HNO_3.

5. If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulfur or sulfides of the tin-group from an alkaline sulfide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or basic hydroxides from solutions in alkalies. These last substances redissolve when the excess of HNO_3 is added.

6. An acid reaction of the aqueous solution towards litmus is due to hydrogen-ion, which may arise from free acid, from an acid salt of a strong acid, or (by hydrolysis) from a neutral salt of a strong acid and a weak base. An alkaline reaction is due to hydroxide-ion, which may arise from a soluble hydroxide, or (by hydrolysis) from a carbonate, sulfide, phosphate, borate, cyanide, or a salt of some other weak acid.

7. When the acid is added to the aqueous solution, the evolution of any gas and its odor should be noted, since this indicates the nature of the acidic constituents present. Thus carbonates effervesce with evolution of CO_2; sulfides produce the odor of H_2S; sulfites and thiosulfates, that of SO_2; and cyanides, that of HCN.

8. There are certain compounds (especially those of antimony and tin, the oxides of iron, MnO_2, and $BaCrO_4$) which dissolve more rapidly or in larger quantity in HCl than in HNO_3. When a substance fails to dissolve completely in the dilute HNO_3 and seems likely from its appearance or behavior to contain any of these compounds, it is therefore well to attempt to prepare an HCl solution of it by proceeding as follows: To a fresh 1 g. sample of the finely powdered substance in a small flask add just 5 cc. 6–normal HCl; heat the mixture

nearly to boiling for 3–4 minutes, covering the flask with a watch-glass to prevent evaporation; and then add 10 cc. water. If the substance has dissolved completely, reject the HNO_3 solution and residue, and treat the HCl solution by P. 21. Otherwise, reject the HCl solution and residue, and treat the HNO_3 solution and residue by P. 3.—As to the reasons for recommending the use of HNO_3, rather than of HCl, as the usual procedure, see Note 4, P. 3.

9. The following general statements may be made in regard to the solubility of substances in water and dilute acids:

All the ordinary salts of sodium, potassium, and ammonium are readily soluble in water.

The salts of mercurous and mercuric mercury, bismuth, antimony, and tin are hydrolyzed by water with precipitation of basic salts, which dissolve readily in dilute HNO_3 or HCl.

The nitrates, nitrites, chlorates, and acetates of all the elements are readily soluble in water (except certain basic nitrates and acetates).

The hydroxides, carbonates, phosphates, borates, arsenates, and arsenites of all the elements except the alkalies are only slightly soluble in water, but dissolve readily in dilute HNO_3 or HCl. ($Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are, however, fairly soluble in water.)

The chlorides, bromides, iodides, and thiocyanates of all the elements except lead, silver, and mercury, and the sulfates of all the elements except calcium, strontium, barium, lead, mercury, and silver are readily soluble in water. (In regard to the solubility of these and other salts of the alkaline earths and of silver and lead, see the Table of Solubilities of Slightly Soluble Substances on page 124.)

Procedure 3.—*Treatment of Non-Metallic Substances not dissolved by Dilute Nitric Acid and of Alloys.*—If the substance is non-metallic and has not dissolved in dilute HNO_3, to the mixture obtained in P. 2 add 5 cc. 16–normal HNO_3, and evaporate just to dryness.

If the substance is an alloy, convert it into a form offering a large surface and treat 0.5 g. of it in a casserole with 10 cc. 6–normal HNO_3. Cover the dish with a watch-glass, heat the mixture nearly to boiling as long as any action continues, adding a little 16–normal HNO_3 if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at 100–130° until it is perfectly dry, by keeping the casserole in motion over a small flame. Loosen the residue from the dish and rub it to a fine powder with a pestle; add to it just 5 cc. 6–normal HNO_3, cover the dish, and warm the mixture, taking care that none of the acid evaporates. Dilute with 20 cc. water, heat to boiling, and note whether there is any residue (see Note 7). If there is a residue, filter it out and wash it. (Residue, P. 4; solution, P. 11.)

Notes.—1. On heating the HNO_3 solution, the presence of sulfides is indicated by the separation of sulfur as a spongy or pasty mass, which floats on the surface and may be removed by means of a spatula or rod; and the presence of iodides is shown by the liberation of free iodin, which may separate as a black precipitate, which imparts a brown color to the solution, and which gives rise to violet vapors above it.

2. When a silicate is decomposed by acid, silicic acid may separate as a gelatinous precipitate, but even then a part of it always remains in solution, mainly as a colloid. When thoroly dried at 100–130°, it is partially dehydrated and becomes entirely insoluble. The HNO_3 acid solution is therefore evaporated to dryness and the residue is heated at 100–130°, in order to remove the silica at this point; for, if it were not removed, it would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by NH_4OH together with the iron group and might then be mistaken for aluminum hydroxide. In the case of nonmetallic substances which cannot contain silica, the heating may be omitted.

3. If the substance is nonmetallic, the residue insoluble in HNO_3 probably consists of one or more of the substances whose formulas are given in Table I under *a* and *b*. Other less common insoluble substances are anhydrous chromium salts, phosphate of tin, ferrocyanide of iron, and silicon carbide.

4. In dissolving nonmetallic substances HCl may be used in place of HNO_3. Each of these acids has advantages and disadvantages of its own, as follows: HNO_3 dissolves, owing to its oxidizing power, many sulfides not attacked by HCl, but fails to dissolve certain substances, especially MnO_2, Sb_2O_5, H_2SnO_3, and $BaCrO_4$, which dissolve in HCl. HCl may cause the precipitation of chlorides of the silver group; while strong HNO_3 on heating oxidizes sulfides partially to sulfates, and may cause the precipitation of lead, barium, strontium, and calcium sulfates; thus in either case making it sometimes impossible to determin whether complete decomposition has resulted. HNO_3 oxidizes mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently almost all the antimony and tin will usually be found in the residue insoluble in dilute HNO_3 after evaporation, all the mercury will be in the H_2S precipitate, and sulfur will always be precipitated by H_2S when iron is present. When HCl is used as a solvent, mercury and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of nonmetallic substances and for the isolation of the silver group, the use of HNO_3 is here recommended.

5. Alloys can not ordinarily be powdered by grinding in a porcelain or agate mortar. They may usually be converted into a form that offers a large surface by hammering in a steel mortar, filing with fine steel file, shaving with a knife, or converting into turnings with a lathe. Only 0.5 g. of an alloy is taken for analysis; for, owing to the absence of acidic constituents, the same quantity of basic elements is contained in a smaller amount of substance.

6. By the treatment of alloys with strong HNO_3, all the more common elements are dissolved by strong HNO_3 except antimony, tin, and silicon. These are oxidized to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid (H_2SiO_3), which separate at once as white amorphous precipitates when considerable amounts of these elements are present. Certain

nitrates, especially that of lead, may separate in crystalline form from the strong HNO_3, but these dissolve upon adding water and heating to boiling.

7. In the case of an alloy the evaporation to dryness and heating at 100–130° serve to partially dehydrate the hydroxides of silicon, tin, and antimony, whereby they are rendered nearly insoluble in HNO_3. This makes possible a conclusion in regard to their presence or absence. Thus, if after having thoroly dried the mixture at this temperature there is no residue insoluble in the HNO_3, it shows the absence of silicon and tin in quantity as large as 1 mg., and that of antimony in quantity as large as 2 or 3 mg. The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand 2 or 3 minutes, and note whether there is any residue whatever. The knowledge that tin is absent enables the subsequent procedures for the detection of this element to be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mg. are not to be tested for. In addition to the hydroxides named above, the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of the substances already mentioned.

8. The hydroxides of antimony, tin, and silicon usually separate also in the treatment of nonmetallic substances with HNO_3 when the corresponding elements are present; but the nonexistence of a residue must not, except in the case of silicon, be regarded as conclusiv evidence of their absence in such substances. For the presence of certain acidic constituents, such as chloride or sulfate, may cause a considerable quantity of tin or antimony to dissolve.

9. A black or metallic residue insoluble in HNO_3, obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

Procedure 4.—*Treatment of the Residue Insoluble in Nitric Acid.*—To the residue insoluble in HNO_3 (P. 3) in a casserole add gradually 5 cc. 12–normal HCl, and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in HCl, add to the mixture without filtering a few drops of 16–normal HNO_3, and heat gently as long as action continues, adding more of the acids if necessary.

Evaporate this solution in HCl alone, or in HCl and HNO_3, without filtering off any residue, just to dryness, taking care not to overheat the dry residue. Add to the residue 5 cc. 6–normal HCl, measured in a small graduate, and 10 cc. water; boil gently for a few minutes if there is a residue: filter, wash the residue thoroly with boiling water, and treat it by P. 5 (or P. 7). Unite the filtrate with the

HNO_3 solution obtained in P. 3 after treating the latter by P. 11; neutralize half the acid in the mixture by adding just 5 cc. 6-normal NH_4OH; and, without filtering off any precipitate, treat the mixture by P. 21.

Notes.—1. Of the substances that may be present in the residue undissolved by HNO_3 (see Table I), the peroxides of manganese and lead and the chromates of barium and lead are reduced and dissolved by concentrated HCl. Antimonic acid ($HSbO_3$) and stannic acid (H_2SnO_3) are also dissolved by it. Upon the addition of HNO_3, whereby the strongly oxidizing mixture known as *aqua regia* is produced, gold, platinum, and mercuric sulfide are entirely dissolved; and silver compounds, such as AgBr, AgI, and AgCN, are converted into AgCl. The chloride of silver and the sulfates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount of dilute HCl added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method of getting them into solution.

2. The solution is evaporated to remove the large quantity of acid which would otherwise interfere with the H_2S precipitation. Care is taken not to overheat the dry residue, so as to avoid loss of mercury, antimony, and tin by volatilization of their chlorides. A measured quantity of HCl is then added; and, after mixing this HCl solution with the HNO_3 solution, an equivalent quantity of NH_4OH is added, in order to produce the acid concentration required for the H_2S precipitation. Only 10 cc. of water are added to the HCl solution at first, so as to prevent the precipitation of SbOCl and thus make it possible to determin whether the substance has been completely decomposed.

3. If the original substance was an alloy, a residue after the treatment with HCl and HNO_3 is likely to consist of metastannic or silicic acid or of carbon, a platinum metal, or an alloy of iron with chromium, silicon, etc. It is best treated with H_2SO_4 and HF by P. 5, in order to test for and remove silica and to dissolve metastannic acid and iron-alloys. If a black or metallic residue still remains, it may be tested for graphite by rubbing a dried portion on the fingers or on paper; and to bring it into solution the remainder may then be fused with Na_2O_2 in a nickel crucible, the mass treated with water and HCl, and the solution analyzed as usual, except that nickel cannot be tested for.

4. If the original substance was an alloy and a large, nonmetallic residue remains after treatment with HNO_3 (P. 3), it is sometimes advantageous, instead of treating it by P. 4, to analyze the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved: Add to the residue in a casserole 3-4 cc. of 96 % H_2SO_4 and heat under the hood until the acid has evaporated to a volume of about 2 cc. Cool, add an equal volume of water, cool again, add 5 cc. HCl to dissolve antimonic oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 cc. ammonium monosulfide, 1 cc. ammonium polysulfide, and 10 cc. 15-normal NH_4OH in a flask. Cover the flask and digest for a few minutes on a steam bath. Filter out the precipitate, which

may consist of small quantities of sulfides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with HCl. Shake to coagulate the precipitate, filter, and wash with hot water. Analyze the precipitate for the tin-group by P. 41; reject the filtrate or test it for phosphate by P. 104.

***Procedure 5.**—*Fluoride Treatment of the Residue Insoluble in the Common Acids.*—Transfer to a platinum crucible (see Notes 1 and 2) the residue after treatment with acids (P. 4), add 2 cc. of 96% H_2SO_4 from a graduate, heat with a moving flame until white fumes are given off, and cool completely.

To test for silicate, add carefully from a lead or hard-rubber tube capped with a rubber nipple pure 48% HF drop by drop until 5–6 drops have been added, and warm the mixture over a steam bath. (Formation of gas bubbles, presence of SILICA or SILICATE.)

Then add 2–5 cc. more pure 48% HF, cover the crucible with a platinum cover, digest on a steam bath for about 15 minutes unless the residue dissolves more quickly; remove the cover, and evaporate under a hood until dense white fumes of H_2SO_4 are given off, taking care to avoid spattering. (See Note 3.) [Unless it is known from the presence of solid substance at this point or from other indications that the residue treated with H_2SO_4 and HF contained other constituents than silica, determin this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the dry residue. If a significant residue remains, add from a graduate 1.5 cc. of 96% H_2SO_4, and heat until the residue is redissolved, not allowing the acid to evaporate.] Cool, pour the contents of the crucible into 10 cc. water, and rinse out the contents with a little water. Boil to dissolve slowly dissolving sulfates; cool, shake, filter, and wash the residue, first with 6-normal H_2SO_4 and then with a little water. (Residue, P. 6; filtrate, P. 11.)

Notes.—1. *A student using this procedure for the first time should work under the direct supervision of an instructor. Great care must be taken not to breathe the fumes of HF nor to get it on the hands; for it is extremely irritating and produces dangerous burns.*

2. *Whenever a residue or precipitate has to be transferred from a filter to a crucible in which it is to be ignited or fused, it is best to separate it as far as possible from the filter-paper, and then to incinerate the part of the paper to which much residue adheres by rolling it up, winding a platinum wire around it in the form of a spiral, and heating it in a gas-flame till the carbon is all burnt off.*

3. *When a liquid is to be evaporated in a crucible, it is well to heat it within a larger iron crucible, which serves as an air-bath. The smaller crucible may be supported upon a nichrome triangle set into holes bored in the side of the iron crucible, or upon a circular disk of asbestos-board with a round hole cut out in the middle and slots cut out along the sides.*

---

* If the use of a platinum crucible or of hydrofluoric acid is impracticable, the less satisfactory, alternativ method described in P. 7 may be employed (see Note 8, P. 5).

4. The test for silica or silicate depends on the formation of SiF_4 gas, which is insoluble in strong H_2SO_4, but dissolves in water in the presence of HF with formation of fluosilicic acid, H_2SiF_6. With free silica the evolution of gas takes place in the cold; but with slowly decomposing silicates, such as feldspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and H_2SO_4, and, of course, do not show the test for silica at this point. The test is delicate enough to enable 1 mg. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with H_2SO_4, an evolution of gas with HF is not produced with the compounds of any element other than silicon. It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if a strongly alkaline solution has been boiled in glass vessels.

5. Since glass and porcelain consist of silicates which are readily attacked by HF, this acid must not be allowed to come into contact with these materials. In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Care must be taken not to introduce into a platinum vessel any solution containing chlorin or bromin or any acid mixture containing nitrates and chlorides by which chlorin would be evolved. Platinum is so slowly attacked by hot concentrated H_2SO_4 that even when 2–3 cc. of the acid are rapidly evaporated in a crucible less than 0.5 mg. passes into solution.

6. The digestion with HF decomposes most silicates and dissolves silica. The subsequent evaporation with H_2SO_4 expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the HNO_3 and HCl. The H_2SO_4 solution is diluted with a small quantity of water so as to cause the complete precipitation of $BaSO_4$, $SrSO_4$, and $PbSO_4$. These sulfates are moderately soluble in strong H_2SO_4 and may not appear till after dilution. The addition of much water is avoided, since $SrSO_4$ and $PbSO_4$ are somewhat soluble in water; and the residue is washed with dilute H_2SO_4 for the same reason. The solution is boiled so as to dissolve anhydrous sulfates, such as those of aluminum and iron.

7. The residue insoluble in dilute H_2SO_4 contains as sulfates all the barium, strontium, and lead, and all of the calcium in excess of 5–10 mg., left undissolved by HNO_3 and HCl; more or less of the chromium (according as the H_2SO_4 has been more or less strongly heated) as a pink anhydrous sulfate; and part of the bismuth as basic sulfate and antimony as antimonic hydroxide, when much of these elements was left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following: silver chloride; corundum, Al_2O_3; chromite, $FeCr_2O_4$; cassiterite, SnO_2; some anhydrous silicates and fluosilicates, such as cyanite or andalusite (Al_2SiO_5) and tourmalin; graphite and carbides; and certain compounds of the rarer elements. For a method of bringing some of these substances into solution, see Note 3, P. 7.

8. If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in HCl and HNO_3 may be fused in a nickel crucible with

Na_2CO_3, as described in P. 7, instead of being treated by P. 5–6. This is, however, a far less satisfactory method of analysis for the following reasons. Compounds of the alkali elements are used as a flux; nickel is introduced from the crucible; and mercury compounds are volatilized;—so that these elements can not be tested for in the subsequent analysis. Moreover, the treatment with HF and H_2SO_4 is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with Na_2CO_3 solution (P. 6). A fusion in a platinum crucible with Na_2CO_3 would be less objectionable; but this is not possible, unless elements reducible to the metallic state are known to be absent in the residue (see Note 5, P. 7).

Procedure 6.—*Treatment of the Residue from the Fluoride Treatment.*—Transfer the residue insoluble in dilute H_2SO_4 (P. 5) to a casserole, add about 25 cc. 3-normal Na_2CO_3 solution, cover the casserole, and boil gently for 10 minutes. Filter and wash the residue thoroly. (Filtrate, reject.) Heat the residue with just 5 cc. HNO_3 and 10–20 cc. water. Filter out any undissolved residue, and treat the solution by P. 11, subsequently testing it only for lead, bismuth, chromium, barium, strontium, and calcium.

Notes.—1. The boiling with Na_2CO_3 converts into carbonates the sulfates of lead, calcium, strontium, and bismuth completely, and at least 80% of the sulfate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes $BaSO_4$. The carbonates dissolve readily in HNO_3. Anhydrous chromic sulfate, which is left undissolved by dilute H_2SO_4 (P. 5) as a fine pink or gray powder, is slowly changed by boiling with Na_2CO_3 to a greenish blue hydroxide which dissolves in the HNO_3, leaving behind the still undecomposed sulfate. Antimonic oxide dissolves only to a small extent (2–4 mg.) in the Na_2CO_3 solution or in the dilute HNO_3.

2. Any residue insoluble in HNO_3 can therefore consist only of barium or chromic sulfate, of antimonic oxide, or of some of the original substance still undecomposed, which is likely to consist of one of the nativ oxides or silicates mentioned in P. 5, Note 7. If such a residue is obtained, it can ordinarily be rendered soluble by fusion with Na_2CO_3 and KNO_3, as described in P. 7; but in this case a platinum crucible may be used for the fusion, provided the residue be first heated with HCl to extract any Sb_2O_5 that may be present and provided silver is not found present in the H_2SO_4 solution obtained in P. 5.

Procedure 7.—*Alternativ Treatment of the Residue Insoluble in the Common Acids.*—If the use of HF (P. 5) is impracticable, transfer the residue insoluble in acids (P. 4) to a nickel crucible (see Note 2, P. 5), heat until the residue is dry, mix the residue with ten to twenty times its weight of anhydrous Na_2CO_3, cover the crucible, heat strongly over a powerful burner, preferably within a cylinder of asbestos-paper, so that complete fusion takes place, and continue the heating for 10–20 minutes. If dark particles of undecomposed substance can still be seen, add gradually in small portions 0.1–0.5 g. of solid KNO_3, and heat strongly for several minutes. Cool, boil the crucible and its contents with water until the fused mass is disintegrated, filter, and wash the residue thoroly. Warm the residue with HNO_3 until action ceases, and filter out any still undecomposed substance.

Test one half of the carbonate solution for acidic constituents as described in the third and fourth paragraphs of P. 131.

Mix a tenth of the HNO_3 solution with a tenth of the carbonate solution, making the mixture acid with HNO_3, if it is not already so. If no precipitate forms, mix the remainder of the acid solution with the remainder of the carbonate solution. Add 3–5 cc. HCl (or more if the solution is still alkaline), and filter. Test the precipitate for lead and silver by P. 13–14. Evaporate the solution, and heat the residue until it is thoroly dry at 120–130° by keeping it in motion over a small flame. Moisten the residue with 16-normal HNO_3, and heat again till the residue becomes perfectly dry. Add from a graduate just 5 cc. 6-normal HNO_3 and about 20 cc. water, and heat to boiling. Filter out any residue, dilute the filtrate to 100 cc., and treat it by P. 21.

If a precipitate forms on mixing the small portions of the HNO_3 solution and the carbonate solution, treat these solutions separately as described in the preceding paragraph, uniting the precipitates formed by the same group-reagent in the subsequent analysis.

Notes.—1. Upon fusion with sodium carbonate most compounds undergo metathesis, the acidic constituent of the compound combining with the sodium, and the basic element with the carbonate. The carbonate formed is, however, sometimes decomposed by heat with production of the oxide or of the metal itself. Acid-forming oxides, such as SiO_2, As_2O_5, and less rapidly Al_2O_3, expel CO_2 from the carbonate and form sodium salts. Such reactions are illustrated by the following equations:

$$\begin{aligned}
BaSO_4 &+ Na_2CO_3 = Na_2SO_4 + BaCO_3.\\
Fe_2SiO_5 &+ Na_2CO_3 = Na_2SiO_3 + Fe_2O_3 + CO_2.\\
4AgCl &+ 2Na_2CO_3 = 4NaCl + 4Ag + 2CO_2 + O_2.\\
SiO_2 &+ Na_2CO_3 = Na_2SiO_3 + CO_2.
\end{aligned}$$

After the treatment with water, the acidic constituent of the substance is therefore found with the excess of carbonate in the aqueous extract, while the basic element remains undissolved by the water and passes into the acid solution. The first and third reactions are examples of cases where the aqueous and acid solutions must not be mixed, for upon mixing $BaSO_4$ or AgCl would again be formed.

2. Of the basic elements that may be present, all or a part of the arsenic, antimony, tin, aluminum, chromium and manganese are contained in the carbonate solution; and this solution must therefore be analyzed for basic elements. Since this solution may also contain Na_2SiO_3, the solution after the addition of acid is evaporated to dryness, and the residue is heated at 100–130°, in order to dehydrate the silicic acid and render it insoluble. The residue insoluble in HNO_3 after this treatment usually consists only of silicic acid. To prove whether it consists wholly of this acid, it may be treated with H_2SO_4 and HF as described in P. 5.

3. Some substances which are not much acted upon by alkali carbonates alone are readily attacked when an oxidizing substance like KNO_3 is present. Thus, sulfides are converted into sulfates and chromium compounds (such as chromite, $FeOCr_2O_3$) into chromates. A few substances, however, such as the nativ or ignited oxides of tin and aluminum, may be only partially decomposed even by long-continued fusion with the mixed fluxes. Such an undecomposed residue may be fused with KOH in a nickel or silver crucible and the fusion treated first with water and then with HCl. The oxides of aluminum and stannic tin, if finely powdered, dissolve rapidly in fused KOH. The aqueous extract contains the aluminum as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, stannic hydroxide, and of other hydroxides accompanying the aluminum or tin oxides; all of which dissolve in HCl.

4. A few milligrams of nickel are taken up from the crucible by the flux, so that this element, as well as the alkali elements, cannot be tested for later in the analysis. The crucible is, however, so little attacked by the flux that it can be used repeatedly.

5. Whenever it is permissible, it is somewhat better to make the fusion in a platinum crucible, since then no foreign substances are introduced from the crucible. It is not permissible, however, to ignite in platinum vessels compounds of the silver, copper, and tin groups; for these may be reduced to the metal by heating with an alkaline flux. The same is true of sulfur, sulfides, and in the presence of organic matter of phosphates; for all these elements form easily fusible alloys with the platinum, and thus spoil the crucible. Moreover, alkaline hydroxides and strongly oxidizing fluxes (such as peroxides and nitrates) must not be fused in platinum, since they attack it fairly rapidly. Therefore, if the fusion is made in platinum, no more KNO_3 should be added than is necessary.

Procedure 8.—*Destruction of Organic Matter.*—If the closed-tube test (P. 1) has shown the presence of organic matter, powder or cut into small pieces 1–5 g. of the substance (according to the quantity of organic matter present). Add to it in a casserole about 5 cc. of 96% H_2SO_4; warm gently until the substance is well charred; cool; add slowly, with constant stirring, under a hood, 16–normal HNO_3, until violent reaction ceases; warm gently for a few minutes, and then heat more strongly, keeping the dish moving, until the substance is thoroly charred. Cool, again add 16–normal HNO_3 as before, and heat until thick fumes of H_2SO_4 are evolved. Repeat this process till the mixture becomes light-colored and remains so when heated strongly.

If the substance has dissolved completely (or even if it has not, if the use of HF is impracticable), evaporate off the H_2SO_4 under a hood till only 1.5 cc. remains, cool completely, add very carefully 10–20 cc. water, and boil. (If a precipitate separates, filter it off and treat it by P. 6.) Treat the solution by P. 11.

If the substance has not dissolved completely, transfer the mixture to a platinum crucible, evaporate off the H_2SO_4 till only 1.5 cc. remain, cool completely, and treat the mixture by the second and third paragraphs of P. 5.

Notes.—1. This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin and cellulose are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilizing certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determin the proximate constituents of the substance.

2. The residue contains: any substances originally present that have not been attacked by HNO_3 or H_2SO_4, especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulfates of these elements are insoluble in dilute H_2SO_4; all the silica, since silicic acid is dehydrated and made insoluble by heating with H_2SO_4; some of the calcium, bismuth, antimony, and tin, when these elements are present in considerable quantity, since their sulfates (or oxides) are not readily soluble in dilute H_2SO_4; and substantially all of the chromium, since its sulfate is converted into the insoluble anhydrous form.

3. After the organic matter is destroyed, the solution is evaporated to 1.5 cc., in order that the concentration of the acid may be properly adjusted in the subsequent H_2S precipitation.

DETECTION OF THE BASIC CONSTITUENTS.

GENERAL DISCUSSION.

The science of qualitativ chemical analysis treats of the methods of determining the nature of the elements and of the chemical compounds which are present in any given substance. When the presence or absence of the various elements is alone determined, the process is called ultimate analysis; when the chemical compounds of which the substance is composed are identified, it is called proximate analysis. In the analysis of inorganic substances, to which this book is devoted, the object in view is ordinarily an intermediate one—namely, that of detecting the base-forming and acid-forming constituents (called in this book for short the basic and acidic constituents) that are present in the substance. Thus the analysis of a substance consisting of calcium sulfate, zinc chromate, and ferric oxide would show not only that the elements calcium, sulfur, zinc, chromium, and iron were present, but also that the sulfur was in the form of sulfate (not sulfide or sulfite), the chromium in the form of chromate (not of a chromic salt), and the iron in the ferric (not the ferrous) state. The reason for this is that the analysis is carried out by dissolving the substance in water (with aid of acids, if necessary), and by treating the solution so obtained successively with a number of different chemical substances. Now, since the chemical reactions of substances in aqueous solutions are determined by the nature of the ions which they yield, and since the ions correspond to the basic and acidic constituents, it is these constituents whose presence or absence is established.

For detecting the basic constituents a systematic method is employed which consists in adding to an acid solution of the substance in succession ammonium chloride, hydrogen sulfide, ammonium hydroxide and sulfide, and ammonium carbonate. By each of these reagents (which is the name applied to substances added to produce any desired chemical reaction) a group of basic constituents is precipitated. Thus, ammonium chloride precipitates those constituents whose chlorides are only slightly soluble in water; hydrogen sulfide, those whose sulfides are only slightly soluble in dilute acid; ammonium hydroxide and sulfide, those whose sulfides or hydroxides are only slightly soluble in ammoniacal solutions; and ammonium carbonate, those whose carbonates are only slightly soluble in water containing ammonium carbonate. The way in which the basic constituents are thus separated into groups is shown in more detail in Table II on the following page.

TABLE II.—SEPARATION OF THE BASIC CONSTITUENTS INTO GROUPS.

SOLUTION IN DILUTE NITRIC ACID CONTAINING ALL THE COMMON BASIC CONSTITUENTS. *Add* NH_4Cl *(P. 11).*						
Precipitate: Silver-Group (Bi, Sb, Pb, Ag, Hg), as chlorides.* See Table III.	Filtrate. *Saturate with* H_2S *gas (P. 21).*					
	Precipitate: Copper-Group and Tin-Group as sulfides. *Treat with* $(NH_4)_2S_x$ *(P. 22).*		Filtrate: *Add* NH_4OH *and* $\overset{H_2S}{\cancel{(NH_4)_2S}}$ *(P. 51).*			
			Precipitate: Aluminum-Group and Iron-Group, as hydroxides and sulfides. *Dissolve in acid, add* $NaOH$ *and* Na_2O_2 *(P. 52).*		Filtrate: *Add* $(NH_4)_2CO_3$ *(P. 81).*	
	Residue: Copper-Group (Hg, Pb, Bi, Cu, Cd), as sulfides. See Table V.	Solution: Tin-Group (As, Sb, Sn), as ammonium sulfo-salts. See Tables IV and VI.	Filtrate: Aluminum-Group (Al, Cr, Zn), as sodium salts. See Table VIII.	Precipitate: Iron-Group (Mn, Fe, Co, Ni), as hydroxides. See Tables IX and X.	Precipitate: Alkaline-Earth-Group (Ba, Sr, Ca, Mg), as carbonates. See Table XI.	Filtrate: Alkali-Group (NH_4, K, Na), as nitrates, etc. See Table XII.

---

* Bismuth, antimony, and lead are precipitated with the silver-group only when a large quantity is present, and then only partially; mercury is precipitated only when it is in the mercurous state.

PRECIPITATION AND ANALYSIS OF THE SILVER-GROUP.

TABLE III.—ANALYSIS OF THE SILVER-GROUP.

<table>
<tr><td colspan="4">Precipitate: $BiOCl^*$, $SbOCl^*$, $PbCl_2^*$, $AgCl$, Hg_2Cl_2. <i>Treat with HCl (P. 12.)</i></td></tr>
<tr><td rowspan="2">Solution:
$BiCl_3$, $SbCl_3$.
<i>Evaporate, pour into water</i>
<i>(P. 12).</i></td><td colspan="3">Residue: $PbCl_2$, $AgCl$, Hg_2Cl_2. <i>Treat with hot water (P. 13).</i></td></tr>
<tr><td>Solution: $PbCl_2$.
<i>Add H_2SO_4</i>
<i>(P. 13).</i></td><td colspan="2">Residue: $AgCl$, Hg_2Cl_2.
<i>Pour NH_4OH through the filter (P. 14).</i></td></tr>
<tr><td rowspan="2">Precipitate:
$BiOCl$,
$(SbOCl)_2\,Sb_2O_3$</td><td rowspan="2">Precipitate:
$PbSO_4$.</td><td rowspan="2">Black residue:
Hg and $Hg^{Cl}_{NH_2}$</td><td>Solution:
$Ag(NH_3)_2Cl$.
<i>Add HNO_3 (P. 14).</i></td></tr>
<tr><td>White precipitate:
$AgCl$.</td></tr>
</table>

* These precipitates form only when large quantities of bismuth, antimony, and lead are present

Procedure 11.—*Precipitation of the Silver-Group.*—Place the cold solution of the substance (prepared by P. 2, 3, 5, 6, or 8, and containing 5 cc. 6–normal acid in about 25 cc. of solution) in a conical flask, and add to it 10 cc. NH_4Cl solution. (White precipitate, presence of SILVER-GROUP.) Let the mixture stand for 3 or 4 minutes; then filter it. (Precipitate, P. 12; filtrate, P. 21.)

Notes.—1. It is recommended that in general hard-glass conical flasks (the so-called Erlenmeyer flasks of Jena or Bohemian glass), rather than beakers or test-tubes, be employed for holding solutions that are being subjected to the operations of precipitation and heating.

2. Even in cases where it is not essential to add a perfectly definit volume of a reagent, the analyst should make it a practis to measure out the quantity to be added, rather than to pour in an indefinit quantity from the reagent bottle. For this purpose a 10 cc. graduate should be constantly at hand. For adding smaller quantities than 1 cc. a dropper should be used. This may be made by drawing out one end of a short glass tube to a wide capillary and capping the other end with a rubber nipple. When more of a reagent than is needed has been poured into a graduate or other vessel, it should never be poured back into the reagent bottle, owing to the danger of contaminating the reagent.

3. Unless the concentration is specified, it is understood that all salt solutions used as reagents are 1–normal, that is, that they contain one equivalent of salt per liter of solution; also that the acid and base solutions used as reagents (those of HCl, HNO_3, H_2SO_4, HAc, NH_4OH, and $NaOH$) are 6–normal.

4. By one *equivalent* of any substance is meant that weight of it which reacts with one atomic weight (1.008 grams) of hydrogen in any of its compounds or with the weight of any other substance which itself reacts with one

atomic weight of hydrogen. Thus, one equivalent is the quantity in grams corresponding to the following formulas: $1NaOH$, $\frac{1}{2}Ba(OH)_2$, $1HCl$, $\frac{1}{2}H_2SO_4$, $\frac{1}{3}H_3PO_4$, $1NH_4Cl$, $\frac{1}{2}Na_2SO_4$, $\frac{1}{2}CaSO_4$, $\frac{1}{3}FeCl_3$. When a substance may take part either in a reaction of metathesis or in one of oxidation and reduction, its *metathetical equivalent* has to be distinguished from its *oxidation equivalent*. Thus the metathetical equivalent of nitric acid is $1HNO_3$; but its oxidation equivalent (when it is reduced to NO) is $\frac{1}{3}HNO_3$. In this book the term equivalent will always be used to denote the metathetical equivalent.—Note that the number of equivalents of a substance is a certain quantity of it; but that the term normal denotes its concentration, that is, the quantity of it per unit-volume (more specifically, the number of equivalents of it per liter).

5. If NH_4Cl produces no precipitate, it proves the absence of silver and mercurous mercury, but not of lead, bismuth, or antimony, since $PbCl_2$ is fairly soluble in water, and BiOCl and SbOCl are fairly soluble in dilute acid.

6. The solubility of $PbCl_2$ is much smaller in a solution of NH_4Cl or of any other chloride than it is in water owing to the so-called common-ion effect, which may be explained in detail as follows: The mass-action law requires that at a given temperature in all dilute solutions containing lead chloride the ratio of the product of the ion-concentrations[*] $(Pb^{++})\times(Cl^-)^2$ to the concentration $(PbCl_2)$ of the un-ionized salt have the same value; that is, $(Pb^{++})\times(Cl^-)^2\div(PbCl_2)=$ some definit value. Now in all solutions which have been saturated with lead chloride as a result of sufficiently long contact with the solid substance, the concentration of the lead chloride present as such (that is, as un-ionized $PbCl_2$) must evidently have the same value, and therefore in all such saturated solutions the ion-concentration product $(Pb^{++})\times(Cl^-)^2$ must also have the same value; that is, in all solutions saturated at a given temperature with lead chloride, $(Pb^{++})\times(Cl^-)^2=$ some definit value. This particular value which the ion-concentration product has when the solution is saturated is commonly called the *solubility-product*; but the principles involved are less likely to be misunderstood if it be called the *saturation-value of the ion-concentration product*. The saturation-value varies, of course, with the nature of the salt, and with the temperature in the case of a given salt. In the case of lead chloride at 20°, whose solubility in water at 20° will be seen by reference to the Table on page 122 to be 70 milli-equivalents per liter, the saturation-value of the ion-concentration product in these units is evidently $(70)\times(70)^2=343{,}000$, provided the ionization be considered to be complete, as may be assumed to be true in these qualitativ considerations in the case of nearly all neutral salts. Any solution containing lead-ion and chloride-ion in which the ion-concentration product exceeds this saturation-value is evidently supersaturated and tends to deposit the solid substance; and any solution in which the ion-concentration product is less than the saturation-value is evidently undersaturated and tends to dissolve more of the solid substance. Now, when NH_4Cl or HCl is added to a saturated solution of $PbCl_2$ in water, the immediate effect is to increase the value of (Cl^-), and therefore of the product $(Pb^{++})\times(Cl^-)^2$; but the solution becomes thereby supersaturated, and $PbCl_2$ will precipitate out of it until the saturation-value of the product $(Pb^{++})\times(Cl^-)^2$ is restored.

---

[*] In mass-action expressions of this kind, chemical formulas within parentheses denote the *concentrations* of the respectiv substances, that is, the quantities of them per liter of solution.

Procedure 12.—*Extraction of Bismuth and Antimony.*—Pour repeatedly through the filter containing the NH_4Cl precipitate (P. 11) a cold 10 cc. portion of 2-normal HCl (see Note 1). Treat the residue by P. 13. Evaporate the HCl solution in a casserole almost to dryness (see Note 2), add a few drops of water, and pour the solution into a flask containing 100 cc. water heated to 50–70°. (Fine white precipitate, presence of BISMUTH or ANTIMONY.) Test the precipitate for bismuth and antimony by filtering it off and treating it by P. 22 and 23.

Notes.—1. When it is directed to dissolve a precipitate by pouring the solvent repeatedly through the filter, this is best done by pouring a single portion of the solvent from one test-tube through the filter into another test-tube back and forth three or four times. When the solvent is to be used hot (as in P. 13), it should be heated to boiling between each pouring.

2. When it is directed to evaporate a solution almost to dryness or just to dryness, the last part of the evaporation should be carried out by keeping the dish moving over a small flame in such a way as not to overheat the residue.

3. The precipitate is extracted with 2-normal rather than with 6-normal HCl, because $PbCl_2$, AgCl, and Hg_2Cl_2 are much more soluble in the more concentrated acid, owing to the formation of acids with complex anions, such as $H^+{}_2PbCl_4^-$, $H^+{}_2AgCl_3^-$, $H^+{}_2HgCl_4^-$.

4. The white precipitate of BiOCl (bismuth oxychloride) formed on the addition of water is produced by the hydrolysis of $BiCl_3$. If HCl, the other product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution. This quantity increases very rapidly with the acid concentration. For this reason, nearly all the HCl must be removed by evaporation and the solution must be added to a large volume of water. Warm water is used, because the precipitation of BiOCl takes place more rapidly at the higher temperature.

5. Antimony is also completely precipitated as an oxychloride from a HCl solution by the addition of a large quantity of water. If the HCl were diluted only till its concentration became about 1.5 normal, the precipitate would be SbOCl; but, if the HCl is made more dilute than this, as it must be to ensure complete precipitation, the precipitate has the formula $2SbOCl.Sb_2O_3$.

6. The expression for the solubility-product of BiOCl is $(Bi^{+++})\times(O)^{-}\times(Cl^{-}) = \text{const.}$ Acids greatly increase its solubility because their H^+ ion combines with the $O^=$ ion to form water, which is a very slightly ionised substance. Chlorides also increase its solubility; for the increase of (Cl^-) which they directly produce is more than compensated by the decrease of (Bi^{+++}) which arises from the formation of un-ionised $BiCl_3$ (and probably also of complex anions, such as $BiCl_4^-$).

Procedure 13.—*Extraction and Detection of Lead.*—Pour repeatedly through the filter containing the residue undissolved by HCl (P. 12) a 10 cc. portion of boiling water. Wash the residue thoroly with hot water, and treat it by P. 14. Cool the 10 cc. aqueous extract and add to it 10 cc. H_2SO_4 (see Note 3, P. 11). (White precipitate, presence of LEAD.) Confirm the presence of lead by filtering out the precipitate, washing it with a little water, and treating it by P. 34.

Procedure 14.—*Detection of Silver and Mercury.*—Pour repeatedly through the filter containing the residue insoluble in hot water (P. 13) a 5–10 cc. portion of NH_4OH. (Black residue on the filter, presence of MERCUROUS MERCURY.) Acidify the filtrate with HNO_3. (White precipitate, presence of SILVER.) When there is much black residue and little or no white precipitate, treat the residue by P. 15.

Notes.—*1. When two quite different limiting quantities of the reagent are specified (for example, 5–10 cc. as in this procedure), the quantity added should be adjusted to the size of the precipitate.*

2. The black residue that is produced by the action of NH_4OH on Hg_2Cl_2 is a mixture of finely divided mercury with the white mercuric compound $HgClNH_2$. The reaction is expressed by the equation:

$$Hg_2Cl_2 + 2NH_4OH = HgClNH_2 + Hg + NH_4Cl + 2H_2O.$$

The compound $HgClNH_2$ may be considered to be a derivativ of $HgCl_2$, formed by replacing an atom of chlorin by the univalent radical NH_2.

3. An NH_4OH solution contains a considerable proportion of (unhydrated) NH_3; and AgCl dissolves readily in it, owing to the formation of a soluble complex salt, $Ag(NH_3)_2Cl$, which in solution is largely ionized into $Ag(NH_3)_2^+$ and Cl^- ions. This complex cation has so slight a tendency to dissociate into Ag^+ and NH_3 that the ratio of its concentration to that of the simple Ag^+ ion is about 10^7 in a normal solution of NH_4OH.

4. If the $PbCl_2$ was not completely extracted from the NH_4Cl precipitate by boiling water (in P. 13), it is converted into a basic salt ($Pb(OH)Cl$) by the NH_4OH, and may pass through the filter, yielding a turbid filtrate. This basic salt will, however, dissolve on the addition of HNO_3.

Procedure 15.—*Detection of Silver in the Presence of Much Mercury.*—Wash the black residue undissolved by NH_4OH (P. 14), and pour repeatedly through the filter containing it a mixture of 3 cc. HCl and 10 cc. saturated Br_2 solution, at the same time rubbing the residue with a glass rod. Wash the filter, and pour repeatedly through it a 10 cc. portion of NH_4OH. Acidify the solution with HNO_3. (Yellowish-white precipitate, presence of SILVER.)

Notes.—1. When much mercury is present a considerable quantity of silver (5 mg. or more) may be so completely retained in the black residue that scarcely any test for silver is obtained in P. 14. This is probably due to the fact that the AgCl is reduced to metallic silver by the metallic mercury. When much mercury is present it is therefore necessary to test the residue for silver, as described in this Procedure.

2. The bromin converts the mercury in the residue into soluble $HgBr_2$ and the silver into insoluble AgBr. The HCl dissolves the $HgClNH_2$ present in the residue with formation of $HgCl_2$.

PRECIPITATION AND SEPARATION OF THE COPPER AND TIN GROUPS.

TABLE IV.—SEPARATION OF THE COPPER AND TIN GROUPS.

<table>
<tr><td colspan="3">HYDROGEN SULPHIDE PRECIPITATE: HgS, PbS, Bi_2S_3, CuS, CdS;
As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5 SnS, SnS_2.
Treat with ammonium polysulfide (P. 22).</td></tr>
<tr><td rowspan="2">Residue: HgS, PbS,
Bi_2S_3, CuS, CdS.
See Table V.</td><td colspan="2">Solution: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$.
Add HCl (P. 23).</td></tr>
<tr><td>Precipitate:
As_2S_5, Sb_2S_5, SnS_2.
See Table VI.</td><td>Filtrate: NH_4Cl.
Reject.</td></tr>
</table>

Procedure 21.—*Precipitation of the Copper and Tin Groups.*—Dilute to 100 cc. the filtrate from the NH_4Cl precipitate (P. 11) or the solution of the substance in HCl (P. 4), which should contain just 5 cc. of 6-normal HNO_3, H_2SO_4, or HCl. Place this solution in a conical flask provided with a two-hole rubber stopper in which is a tube leading to the bottom of the flask. Pass into it in the cold a slow current of H_2S, until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of H_2S. Filter at once, wash the precipitate with hot water (see Note 1), and treat it by P. 22. Heat the filtrate nearly to boiling (to 70–90°), and pass H_2S into it at that temperature for 5–10 minutes.

If there is no further precipitate, treat the solution by P. 51.

If there is a further precipitate, evaporate the mixture almost to dryness. Add 3–5 cc. 12-normal HCl and evaporate just to dryness, to destroy the HNO_3. Then add 10 cc. 6-normal HCl, saturate the cold solution with H_2S, heat it to 70–90°, and pass H_2S into it for 5–10 minutes. Cool the mixture, dilute it to 100 cc., and saturate it with H_2S. Filter out the precipitate, wash it, treat it by P. 22, and unite the residue and the solution with those coming from the first H_2S precipitate. Treat the filtrate by P. 51.

Notes.—1. The washing of precipitates should in general be continued until the wash-water will no longer giv a test for any substance known to be present in the filtrate (for example, in this case for acid with blue litmus-paper or for chloride with $AgNO_3$). Precipitates which are practically insoluble in water (like all the sulfides and hydroxides that are met with in this System of Analysis) are best washed with nearly boiling water, as this runs through the filter more rapidly and extracts soluble substances more readily. Precipitates which are appreciably *soluble should be washed with cold water and with only a small quantity of it. The proper method of washing a precipitate is to cause a fine stream of water from a wash-bottle to play upon the upper edge of the filter. The wash-water should in general not be allowed to run into the filtrate, so as not to dilute it unnecessarily. When, however, a considerable proportion of the solution is likely to be retained in the filter and precipitate, it is well to add the first washings to the filtrate.*

2. The formation of a white precipitate on diluting the solution to 100 cc. shows the presence of much bismuth or antimony. The precipitate, which consists of BiOCl or SbOCl, need not be filtered off. The formation, on passing in H_2S, of a white or yellowish precipitate which immediately turns black with more H_2S indicates mercury. (The white compound is $HgCl_2.2HgS$, and this is converted into black HgS by the excess of H_2S.) The formation of an orange precipitate shows antimony; of a yellow one, cadmium, arsenic, or stannic tin. All the other sulfides are black.

3. The solution is afterwards heated nearly to boiling and again saturated with H_2S, in order to ensure the detection of arsenic; for this element, when present in the higher state of oxidation (as arsenic acid) is only very slowly precipitated by H_2S in the cold. At 70–90° the precipitation is much more rapid, especially if the solution has been previously saturated with H_2S in the cold. Under these conditions even 1 mg. As givs a distinct precipitate in less than 5 minutes. Continuous treatment with H_2S at 70–90° in an open vessel does not, however, completely precipitate a large quantity of arsenic from such a weakly acid solution even within an hour. For this reason, when a considerable precipitate forms in the hot solution, it is directed to evaporate the filtrate, to add HCl to destroy the HNO_3 (which in the concentrated state would decompose the H_2S), to dissolve the residue in HCl, and to pass H_2S through the hot solution. From this concentrated acid solution the arsenic precipitates completely in 5–10 minutes. The reasons for this peculiar behavior of arsenic in the higher state of oxidation are presented in Note 2, P. 43. The solution is finally diluted and saturated in the cold with H_2S, since the other elements are not completely precipitated until the arsenic has been removed.

4. The effect of acid on the precipitation of the sulfides is explained by the mass-action law and ionic theory as follows: When a dilute solution, whether aqueous or acid, is saturated at a definit temperature with H_2S gas under the atmospheric (or any definit) pressure the H_2S present as such always has the same concentration. This ionizes, however, to a slight extent into H^+ and HS^-, and to a still less extent into $2H^+$ and $S^=$. It is only the latter form of ionization that needs to be considered here. Now between the H_2S and its ions must be maintained the equilibrium expressed by the equation $(H^+)^2 \times (S^=) = \text{const.} \times (H_2S)$; or, since in this case $(H_2S) = \text{const.}$, as just stated, it follows that also $(H^+)^2 \times (S^=) = \text{const.}$ From this it is evident that when (H^+) is increased by the addition of acid to the solution, $(S^=)$ must be decreased in the proportion in which the square of (H^+) is increased; thus, if (H^+) is doubled, $(S^=)$ will be reduced to one-fourth. But in order that a sulfide—for example, of the formula $M^{++}S^=$—may precipitate, the concentration-product $(M^{++}) \times (S^=)$ must attain its saturation-value. This value varies, however, with the nature of the sulfide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when (M^{++})

has a definit value (for example, 1 mg. in 100 cc.) will be different for different sulfides and for the same sulfide at different temperatures. Thus if the elements are arranged in the order in which they are precipitated from cold HCl solutions as the acid-concentration is progressivly decreased, the series is approximately as follows: arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. The acid concentration which permits precipitation also varies with the ionization of the acid; thus zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionization of this acid, the H^+ concentration is less than in a far more dilute solution of HCl. The three acids, HCl, HNO_3, and H_2SO_4, do not, however, differ greatly in this respect, since they are all largely ionized in dilute solution.

5. The acid concentration is made 0.3 normal (5 cc. of 6–normal acid being present in 100 cc.) and the solution is saturated with H_2S gas in the cold, since under these conditions even 1 mg. of cadmium, lead, or tin precipitates, and even 300 mg. of zinc remain in solution. (This statement in regard to zinc is true, however, only when the solution contains also a considerable quantity of chloride-ion, such as was added in P. 11, and when it is not allowed to stand.) Moreover, even when a small quantity of any of the iron-group elements is present with a large quantity of a copper-group element, the former is not carried down in the H_2S precipitate under these conditions to such an extent as to prevent its detection in the filtrate, provided as much of it as 1 mg., or in some combinations as much as 2 mg., is present.

6. A white, finely divided precipitate of free sulfur will be formed if the solution contains substances capable of oxidizing H_2S. The most important of these likely to be present are ferric salts, chromates, permanganates, and chlorates. The reduction by H_2S of ferric salts to ferrous is attended by a change in color from yellow to colorless; of chromates to chromic salts, from orange to green; and of permanganates to manganous salts, from purple to colorless. Nitric acid, if it were fairly concentrated, would also destroy the H_2S; but at the concentration in question (0.3 normal) it has scarcely any oxidizing action even in boiling solution.

7. In balancing equations expressing reactions of oxidation and reduction, like those referred to in the preceding note, the main thing is to determin the number of molecules of the oxidizing and reducing substances which react with one another. This can be done most simply by considering, in the way illustrated by the following examples, the changes which take place in the valences of the atoms of these substances. Thus, in the reduction of a ferric to a ferrous salt by hydrogen sulfide, the iron atom changes in valence from +3 to +2, and the sulfur atom changes in valence from −2 (in H_2S) to zero (in ordinary sulfur). Since the total change in the number of valences must be equal and opposit in the two substances, it is evident that two molecules of ferric salt react with one of hydrogen sulfide, and therefore that the equation is:

$$2FeCl_3 + H_2S = FeCl_2 + S + 2HCl.$$

In the reduction of $HClO_3$ to HCl by H_2S, the chlorin atom decreases in valence from +5 to −1 (thus by six positiv valences); hence there must be a decrease of six negativ valences in the reducing substance, and that this may be the case three molecules of H_2S are evidently required. The equation is therefore:

$$HClO_3 + 3H_2S = HCl + 3S + 3H_2O.$$

In cases where the valence of an atom in a substance is in doubt, it can be found at once from the valences of the other atoms with the aid of the principle that in any compound the sum of all the positiv valences is equal to the sum of all the negativ valences; thus in chloric acid $HClO_3$, since the three oxygen atoms have 6 negativ valences and the hydrogen atom has one positiv valence, the chlorin atom must, in order to make the compound neutral, have 5 positiv valences.

Consider as another example the reduction of potassium permanganate ($KMnO_4$) to manganous chloride ($MnCl_2$) by H_2S in the presence of HCl. The number of valence of the manganese atom is seen to be +7 in $KMnO_4$ (since that of four oxygen atoms is −8 and that of the potassium atom is +1) and to be +2 in $MnCl_2$. The proportion is therefore $2KMnO_4 : 5H_2S$, and the reaction is:

$$2KMnO_4 + 5H_2S + 6HCl = 2MnCl_2 + 2KCl + 5S + 8H_2O.$$

The amount of acid required in such cases can be seen by inspection,—most readily by noting how many hydrogen atoms are needed to combine with the oxygen atoms of the substance undergoing reduction. Thus in this case 16 hydrogen atoms are evidently needed for this purpose; and, since ten are furnished by the H_2S, six more must be supplied by adding 6 molecules of HCl (or an equivalent quantity of some other acid).

Procedure 22.—*Separation of the Copper and Tin Groups by Ammonium Sulfide.*—Transfer the H_2S precipitate (P. 21) to a small casserole, add to it 10–25 cc. ammonium monosulfide (if the original substance was treated with strong HNO_3 in P. 3), or 5–10 cc. ammonium polysulfide (if it was dissolved in water or in dilute HNO_3 in P. 2), cover the dish, and warm the mixture slightly (to 40–60°) for about 10 minutes with frequent stirring. Add 10 cc. water and filter. [If the residue is large and much has been extracted from it by this treatment, as indicated by its appearance or as determined in P. 23, wash it once with hot water, warm it again with ammonium monosulfide or polysulfide, and filter, collecting the filtrate separate from the first one.] Wash the residue thoroly with hot water (see Note 1, P. 21.). (Residue, P. 31; solutions, P. 23.)

Notes.—1. When a small precipitate is to be treated with a solvent, this may be done by pouring a portion of the solvent repeatedly through the filter. When a considerable precipitate is to be so treated, the filter is opened, the portions to which no precipitate adheres are torn off, and the remainder is laid along the side of a casserole; the solvent is then poured over it and is swashed to and fro, the precipitate being rubbed at the same time with a glass rod, so as to remove it from the filter. If this succeeds, the filter is drawn out and thrown away; otherwise, it is allowed to disintegrate and filtered out together with any residue. It is often still better to wash the precipitate off the opened filter by blowing the solvent upon it in a fine stream from a small wash-bottle.

2. The ammonium monosulfide reagent is a solution of $(NH_4)_2S$ and of the products of its hydrolysis, NH_4SH, NH_4OH, and a little H_2S. The polysulfide

reagent contains in addition some of the disulfide $(NH_4)_2S_2$ and of its hydrolysis product $(NH_4)HS_2$. The monosulfide is prepared by saturating concentrated NH_4OH with H_2S gas (whereby NH_4SH is formed), adding an equal volume of NH_4OH, and diluting the solution. The polysulfide is prepared from this solution by dissolving sulfur in it. These reagents, especially the monosulfide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles; for the oxygen of the air destroys the sulfide with liberation of sulfur, which at first combines with the still unchanged sulfide forming the polysulfide, but later precipitates when the oxidation becomes more complete.

3. The chemical action of ammonium sulfide in dissolving the sulfides of the tin-group depends on the formation of soluble salts of sulfoacids with complex anions. When the monosulfide is used, the reactions are as follows:

$$\left\{\begin{matrix} As_2S_3 \\ Sb_2S_3 \end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix} (NH_4^+)_3AsS_3^{---} \\ (NH_4^+)_3SbS_3^{---} \end{matrix}\right\}$$

$$\left\{\begin{matrix} As_2S_5 \\ Sb_2S_5 \end{matrix}\right\} + 3(NH_4)_2S = 2\left\{\begin{matrix} (NH_4^+)_3AsS_4^{---} \\ (NH_4^+)_3SbS_4^{---} \end{matrix}\right\}$$

$$SnS_2 + (NH_4)_2S = (NH_4^+)_2SnS_3^{--}.$$

The disulfide present in the polysulfide oxidizes the lower sulfides (As_2S_3, Sb_2S_3, SnS) to the same sulfosalts as are obtained by dissolving the higher sulfides (As_2S_5, Sb_2S_5, SnS_2) in ammonium monosulfide. It will be seen that these sulfo-salts are analogous to the salts of the familiar oxygen acids of these elements, the difference being that sulfur has replaced oxygen; and they are so named as to indicate this relationship. Thus the five sulfo-salts whose formulas are given above are called ammonium sulfarsenite, sulfantimonite, sulfarsenate, sulfantimonate, and sulfostannate.

4. In separating the copper-group from the tin-group (colorless) ammonium monosulfide is used rather than (yellow) polysulfide whenever the H_2S precipitate must contain in the state of the higher sulfide (SnS_2 or Sb_2S_5) any tin or any antimony that is present. This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water or dilute HNO_3 was used; hence the directions as to the choice between the two solvents. The polysulfide has the disadvantages that it yields a large precipitate of sulfur on acidification and that it dissolves a not inconsiderable quantity of CuS and HgS, thus making it more difficult to determin from the color of the HCl precipitate obtained in P. 23 whether or not elements of the tin-group are present. The fact that it dissolves some CuS and HgS also diminishes the delicacy of the tests for copper and mercury. The polysulfide must, nevertheless, be used if tin may be present as SnS, or much antimony as Sb_2S_3; for in the monosulfide SnS is only slightly soluble, and Sb_2S_3 only moderately soluble.

5. More specifically, the behavior of the various sulfides, when warmed with 10 cc. of these reagents, is as follows: Of the sulfides of the copper-group none dissolves to a significant extent in ammonium monosulfide. 5–10 mg. CuS and 0.5–1.0 mg. HgS may, however, dissolve in the polysulfide when the substance contains a large quantity of these elements. Yet when only 2 mg. are present, either of these elements can be detected in the analysis of the copper-group, even when the polysulfide is used, provided only one treatment with it has

been made. Of the sulfides of the tin-group, 500 mg. of As as As_2S_3 or As_2S_5, of Sb as Sb_2S_5, or of Sn as SnS_2 dissolves in either the monosulfide or polysulfide, and 500 mg. of Sn as SnS or of Sb as Sb_2S_3 dissolve in the polysulfide. Hardly any SnS and only 50–100 mg. Sb as Sb_2S_3 dissolve in the monosulfide.

6. Even when a quantity of only 1 or 2 mg. of arsenic or antimony is present with a large quantity (even 500 mg.) of an element of the copper-group, enough is extracted by either the monosulfide or polysulfide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper-group and only 3–5 mg. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the residue, even when the polysulfide is used. On this account it is necessary to test for tin in the analysis of the copper-group.

Procedure 23.—*Reprecipitation of the Tin-Group.*—Dilute in a small flask the first portion of the ammonium sulfide solution (P. 22) with about 20 cc. water, make it slightly acid with HCl (see Note 2), and shake the mixture for 2 or 3 minutes to coagulate the precipitate. (White or pale yellow precipitate, absence of TIN-GROUP; deep yellow or orange precipitate, presence of TIN-GROUP.—See Notes 4 and 5.) [Treat the second portion of the ammonium sulfide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one.] Filter out and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 41; filtrates, reject.)

Notes.—1. In cases where the filtration is slow, where the precipitate must be washed with very little water, or where (as in this case) it must be freed as far as possible from water, it is advisable to filter with the aid of suction. This operation is carried out by reinforcing the ordinary filter with a small hardened filter placed below it in the funnel, by inserting the funnel in a rubber stopper in the neck of a filter-bottle, and connecting the side arm of the filter-bottle to a suction-pump by means of a rubber tube carrying a screw-clamp. The suction should be applied very gradually so as to avoid breaking the filter. The filtrate should be poured out of the filter-bottle before beginning to wash the precipitate.

2. Whenever it is directed to make a solution slightly acid or alkaline, this should be done carefully as follows: Add from a graduate somewhat less acid or alkali than will neutralize the alkali or acid known to be present in the solution. Then add from a dropper more of the acid or alkali, a drop or two at a time, till a glass rod dipped in the solution and touched to a piece of blue or red litmus paper placed on a watch-glass changes the color of the litmus.

3. When the HCl is added to the solution of the sulfosalts, the corresponding sulfoacids which are liberated decompose immediately into H_2S and the solid sulfides. These are now necessarily in the higher state of oxidation, since the lower sulfides, if originally present, have been oxidized by the polysulfide. The fact that the sulfide precipitates when the solution of the sulfosalt is acidified is a consequence of the mass-action-law. Thus, since the complex anions dissociate according to the equations,

$$SnS_3^{--} = \underline{SnS_2} + S^{--},\quad 2AsS_4^{---} = \underline{As_2S_5} + 3S^{--},\quad 2SbS_4^{---} = \underline{Sb_2S_5} + 3S^{--},$$

this law evidently requires that, in any solution saturated with the solid sulfide, the concentration of the complex anion, and therefore of the tin, arsenic, or antimony in the solution, increase with increasing concentration of the $S^{=}$ ion. Now in the solution of the largely ionized $(NH_4)_2S$ there is a large concentration of $S^{=}$ ion; but when the solution is made acid with HCl, the $S^{=}$ ion is almost completely converted by the relativly large concentration of the H^+ ion into the slightly ionized substances HS^- and H_2S.

4. Much time is ordinarily saved by determining at this point whether or not any element of the tin-group is present. When ammonium monosulfide has been used, there is never any difficulty in drawing a definit conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin-group only a very small, nearly white precipitate of finely divided sulfur separates. Even when ammonium polysulfide has been used, it is usually possible to decide as to the presence or absence of a small quantity of arsenic, antimony, or tin; for, altho considerable sulfur is then liberated, yet the precipitate is distinctly lighter colored and smaller in appearance when it consists only of sulfur than it is when even 1 mg. of arsenic, antimony, or tin is present with the sulfur. The difference is most marked when only a slight excess of HCl has been used in the acidification and when the acidified mixture has been shaken, but not heated. In any doubtful case, the precipitate should be compared with that produced by acidifying 5–10 cc. of ammonium polysulfide to which 1 mg. of arsenic, antimony, or tin has been added.

5. When, however, the HCl precipitate from a polysulfide solution is fairly small and is dark brown (indicating copper) or dark gray or black (indicating mercury) or of unpronounced yellow or orange color, so as to make any conclusion as to the tin-group doubtful, the precipitate is best treated as follows: Heat it with 15–20 cc. NH_4OH almost to boiling for 5 minutes and filter; test the precipitate for copper by P. 31, 35, and 37, if it has not already been found present; add to the filtrate a few drops of ammonium monosulfide, filter out any precipitate, heat the filtrate to boiling, make it acid with HCl, shake, filter out the precipitate, and treat it by P. 41 as usual. The character of the HCl precipitate now obtained will clearly indicate the presence or absence of the tin-group; for by the treatment with NH_4OH the excess of sulfur originally present and any CuS is left undissolved, and by the $(NH_4)_2S$ added to the solution any mercury present is precipitated, so that the HCl precipitate can contain only sulfides of the tin-group and a very little sulfur. As_2S_5, Sb_2S_5, and SnS_2 all dissolve in NH_4OH (tho in the cases of Sb_2S_5 and SnS_2 less abundantly than in ammonium sulfide), owing to the formation of a mixture of salts of partially sulfurated acids, such as H_3AsO_3S and $H_3AsO_2S_2$. The addition of $(NH_4)_2S$ to the NH_4OH solution and the heating serve to convert these into the fully sulfurated acids, such as H_3AsS_4; from which HCl will then precipitate the simple sulfides much more completely.—The incidental removal of the small amounts of CuS and HgS by the NH_4OH treatment is not necessary so far as the analysis of the tin-group is concerned, since their presence does not interfere with the detection of even 1 mg. of arsenic, antimony, or tin; but it does enable 1 or 2 mg. of copper to be detected which might otherwise be lost.—In this connection it may be mentioned that a mixture of SnS_2 and Sb_2S_5 does not always have a color intermediate between the yellow and orange colors of the separate sulfides, but that it may be brown or dark gray.

ANALYSIS OF THE COPPER-GROUP.

Table V.—Analysis of the Copper-Group.

<table>
<tr><td colspan="6">RESIDUE FROM AMMONIUM SULFIDE TREATMENT: HgS, PbS, Bi_2S_3, CuS, CdS.
Boil with HNO_3 (P. 31).</td></tr>
<tr><td colspan="2">Residue: HgS.
Add Br_2 solution (P. 32).</td><td colspan="4">Solution: Pb, Bi, Cu, Cd as nitrates.
Add H_2SO_4, evaporate, add water (P. 33).</td></tr>
<tr><td rowspan="4">Residue: Sulfur.</td><td>Solution: $HgBr_2$.
Add $SnCl_2$.</td><td rowspan="3">Precipitate: $PbSO_4$.
Dissolve in NH_4Ac, add K_2CrO_4 (P. 34).</td><td colspan="3">Filtrate. *Add NH_4OH (P. 35).*</td></tr>
<tr><td rowspan="3">White or gray precipitate: Hg_2Cl_2 or Hg.</td><td rowspan="2">Precipitate: $Bi(OH)_3$.
Add Na_2SnO_2. (P. 36).</td><td colspan="2">Filtrate: $Cu(NH_3)_4SO_4$, $Cd(NH_3)_4SO_4$.</td></tr>
<tr><td>*To a small part add HAc and $K_4Fe(CN)_6$ (P. 37).*</td><td>*To the remainder add KCN and H_2S (P. 38).*</td></tr>
<tr><td>Yellow precipitate: $PbCrO_4$.</td><td>Black residue: Bi.</td><td>Red precipitate: $Cu_2Fe(CN)_6$.
White precipitate: $Cd_2Fe(CN)_6$.</td><td>Yellow precipitate: CdS.
Solution: $K_3Cu(CN)_4$.</td></tr>
</table>

Procedure 31.—*Treatment of the Sulfides with Nitric Acid.*—To the residue from the ammonium sulfide treatment (P. 22) in a casserole add 10–20 cc. 2-normal HNO_3 solution, heat to boiling, and boil gently for a minute or two. Filter, and wash the residue. (Residue, P. 32; solution, P. 33.)

Notes.—1. Boiling HNO_3 of this concentration dissolves the sulfides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Only a little HgS is dissolved by this treatment, unless the boiling is long continued.

2. Moderately concentrated HNO_3 dissolves sulfides much more rapidly than HCl or H_2SO_4 of the same concentration; for with the latter acids the sulfide-ion is removed from the solution only by combination with the hydrogen-ion and by the volatilization of the H_2S formed thereby, while with HNO_3 the sulfide-ion (or the H_2S in equilibrium with it) may also be destroyed by oxidation to ordinary sulfur. The oxidizing action of HNO_3 is, however, slow, unless it is hot and as concentrated as 2-normal.

3. That HgS, unlike the other sulfides, does not dissolve in the dilute HNO_3 is doubtless due to the much smaller concentration of its ions in its saturated solution and to the fact that at this small concentration sulfide-ion (or the H_2S in equilibrium with it at a correspondingly small concentration) is oxidized only very slowly by the dilute HNO_3. HgS is, however, readily dissolved by more vigorous oxidizing agents, such as *aqua regia* or bromin solution, since they react rapidly with sulfide-ion (or with H_2S) even when its concentration is very small.

4. If more concentrated HNO_3 be used, or if the acid become concentrated by long boiling, the black HgS is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound ($Hg(NO_3)_2.2HgS$). As a small quantity of HgS may be so converted even by the hot 2-normal HNO_3, the residue should be tested for mercury by P. 32, even if it is light-colored. A light-colored residue must often be tested also for tin (see Notes 2 and 3, P. 32).

5. When much lead, copper, or bismuth is present the sulfur formed generally encloses enough of the undissolved sulfide to give it a black color. A black residue is therefore not necessarily HgS, but must be further tested for mercury as described in P. 32.

6. Some sulfur is always oxidized to H_2SO_4 by the boiling HNO_3; but, even in the presence of much lead, $PbSO_4$ is not precipitated, owing to its moderate solubility in HNO_3.

7. Even when only 1 mg. of lead, bismuth, or copper is present with 500 mg. of mercury, enough of any of these elements is extracted from the residue by the HNO_3 to giv a satisfactory test in the subsequent procedures; but in the case that 1–5 mg. of cadmium are associated with 300–500 mg. of mercury, about four-fifths of the cadmium is retained in the residue, so that a correspondingly small precipitate of CdS is produced in the final test for cadmium, and 1–2 mg. may escape detection.

Procedure 32.—*Confirmatory Test for Mercury.*—Transfer the residue undissolved by HNO_3 (P. 31), with the filter if necessary, to a casserole, add 10–40 cc. saturated Br_2 solution, cover the dish, and warm slightly for 5–10 minutes, with frequent stirring. Boil the mixture until the bromin is expelled, and filter. (Residue, see Note 3.) Cool the solution, and add to it 15–20 drops of HCl and one drop of $SnCl_2$ solution; then add 3–5 cc. $SnCl_2$ solution. (White precipitate turning gray, or gray precipitate, presence of MERCURY.)

Notes.—1. In the final test for mercury HCl is added to prevent the precipitation of a basic tin salt when the $SnCl_2$ reagent is diluted, to diminish the tendency of CuCl to precipitate, and to cause the formation at first of white Hg_2Cl_2. For the last reason, also, a single drop of $SnCl_2$ solution is first added to the cold solution. By the excess of $SnCl_2$ the white precipitate is reduced to gray, finely divided mercury. This darkening of the precipitate distinguishes Hg_2Cl_2 from CuCl, which may separate as a white precipitate if a large quantity of CuS was left undissolved by the HNO_3 in P. 31.

2. If elements of the copper-group are present in large quantity (50–

500 mg.), the residue from the Br_2 treatment should be tested for tin, in order to guard against overlooking the presence of a small quantity of this element in the substance. For, as stated in P. 22, Note 6, a quantity of tin as large as 5 mg. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulfide when this residue is large. Any SnS or SnS_2 present in it is converted by the HNO_3 in P. 31 into metastannic acid (H_2SnO_3), very little of which is dissolved either by the acid or by the Br_2 solution used in P. 32.

3. To recover the tin from the residue, proceed as follows: Digest the residue from the Br_2 treatment, if it is still dark-colored, with another portion of Br_2 solution (to extract the rest of the mercury), filter, reject the filtrate, and warm the residue slightly with 2–5 cc. ammonium monosulfide. Filter, and unite the solution with the main ammonium sulfide solution obtained in P. 22. By this procedure 2 mg. Sn can be detected.

4. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl and adding gradually a little solid $KClO_3$. Metastannic acid, being soluble in HCl, then passes into solution with the mercuric salt, but it does not interfere with the test for mercury.

Procedure 33.—*Precipitation of Lead with Sulfuric Acid.*—To the HNO_3 solution (P. 31) add 10 cc. H_2SO_4 and evaporate in a casserole to a volume of 1–2 cc. until dense white fumes of H_2SO_4 begin to come off. Cool the mixture, and pour it into 10–15 cc. cold water in a test-tube, rinsing the casserole with the same solution. Cool again, shake, and let the mixture stand 5 minutes, but not much longer. (Fine white precipitate, presence of LEAD.) Filter, and wash the precipitate first with H_2SO_4, and finally with a little water. (Precipitate, P. 34; filtrate, P. 35.)

Notes.—1. $PbSO_4$ is somewhat soluble both in water and in concentrated H_2SO_4, but much less so in dilute H_2SO_4, its solubility being scarcely appreciable in the cold 6-normal acid. That the solubility in dilute H_2SO_4 is less than that in water is due mainly to the common-ion effect. Concentrated H_2SO_4 is, of course, an entirely different solvent. $PbSO_4$ dissolves fairly readily in dilute HNO_3, owing to the tendency to form the intermediate HSO_4^- ion; hence, to ensure complete precipitation of $PbSO_4$, the HNO_3 must be removed by evaporation. To ensure complete precipitation it is also necessary to let the mixture stand a few minutes; for the solutions of substances which, like $PbSO_4$, are crystalline and appreciably soluble tend to remain supersaturated.

2. When much bismuth is present it ordinarily dissolves at first when the water is added to the concentrated H_2SO_4, provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxysulfate, such as $(BiO)_2SO_4$, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mg. of bismuth. If the precipitate is of this character, free it from bismuth before applying the confirmatory test for lead by pouring repeatedly through the filter a 5–10 cc. portion of HCl and treating the solution so obtained by P. 33. The evaporation with H_2SO_4 is necessary in order to ensure reprecipitation of the $PbSO_4$ that has been dissolved by the HCl.

Procedure 34.—*Confirmatory Test for Lead.*—Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 33) a 10–20 cc. portion of NH_4Ac solution. (See Note 1, P. 12.) To the filtrate add a few drops of K_2CrO_4 solution and 2–5 cc. HAc. (Yellow precipitate, presence of LEAD.)

Notes.—1. This confirmatory test for lead should not be omitted; for the H_2SO_4 precipitate may consist not only of $PbSO_4$ but of $(BiO)_2SO_4$ or of $BaSO_4$, which last closely resembles $PbSO_4$ in appearance. $(BiO)_2SO_4$ dissolves in NH_4Ac solution and gives a yellow precipitate on adding K_2CrO_4; but this precipitate, unlike $PbCrO_4$, dissolves readily in acetic acid.

2. The solubility of $PbSO_4$ in NH_4Ac solution depends on the formation by metathesis of undissociated $PbAc_2$, this salt being much less ionized than most other salts of the same valence-type. On the addition of a chromate to this solution the much more difficultly soluble $PbCrO_4$ is precipitated. $BaSO_4$ is not dissolved by NH_4Ac solution, owing to its very slight solubility in water and the fact that barium acetate, unlike lead acetate, is a largely ionized salt.

Procedure 35.—*Precipitation of Bismuth with Ammonium Hydroxide.*—To the H_2SO_4 solution (P. 33) add NH_4OH slowly until a strong odor of it persists after shaking. (White precipitate, possible presence of BISMUTH; blue solution, presence of COPPER.) Shake to cause coagulation, filter, and wash the precipitate thoroly. (Precipitate, P. 36; filtrate, P. 37 and 38.)

Notes.—1. The precipitate produced by NH_4OH may consist also of $Fe(OH)_3$, or of other hydroxides of the iron-group, if these elements were carried down in the H_2S precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory test of P. 36 must be applied.

2. $Cd(OH)_2$ or $Cu(OH)_2$, tho only very slightly soluble in water, dissolves in NH_4OH owing to the combination of the Cd^{++} or Cu^{++} ion present in the saturated solutions with NH_3, forming the complex cation $Cd(NH_3)_4^{++}$ or $Cu(NH_3)_4^{++}$. These complex cations have an extremely small ionization tendency; thus in a normal NH_4OH solution the ratio of the concentration of the complex cadmium ion to the simple cadmium ion is about 10^7. The solubility of these hydroxides in NH_4OH is greatly increased by the presence of ammonium salts, since these salts, owing to the common-ion effect, greatly reduce the ionization of the NH_4OH, and therefore the OH^- concentration in the solution, thus enabling the Cd^{++} or Cu^{++} concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of $Cd(OH)_2$ or $Cu(OH)_2$ in NH_4OH alone.

Procedure 36.—*Confirmatory Test for Bismuth.*—Pour through the filter containing the well washed NH_4OH precipitate (P. 35) a cold freshly prepared solution of sodium stannite (see Note 1). (Black residue, presence of BISMUTH.)

Notes.—1. The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding NaOH solution, a few drops at a time, to 1 cc. $SnCl_2$ reagent diluted with 10 cc. water, cooling the mixture in running water after each addition, until the large precipitate of $Sn(OH)_2$ first formed is dissolved and a clear or slightly turbid liquid results. The solution must be kept cold while it is being prepared, and it must be freshly prepared, because the stannite decomposes spontaneously into stannate (Na_2SnO_3) and metallic tin, and because it oxidizes in contact with air to sodium stannate. SnO_2H_2 is an example of a so-called amphoteric substance—one which acts either as a base or an acid, as is shown by its solubility in both acids and alkalies.

2. The final test with sodium stannite depends on the reduction of $Bi(OH)_3$ to black metallic bismuth. The test is an extremely delicate one. The other reducible substances, like $HSbO_3$, $Fe(OH)_3$, $Pb(OH)_2$, or $Cu(OH)_2$, that might possibly be present in the NH_4OH precipitate are not reduced by short contact with stannite solution in the cold. Mercury, if present, would cause blackening; but it is not precipitated by NH_4OH in the presence of ammonium salt.

Procedure 37.—*Confirmatory Test for Copper.*—Acidify one-fourth of the NH_4OH solution (P. 35) with HAc, add one drop $K_4Fe(CN)_6$ solution, and allow the mixture to stand for 2 or 3 minutes. (Red precipitate, presence of COPPER.) Then add 4–5 cc. more $K_4Fe(CN)_6$ solution. If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink color on the filter, presence of COPPER.)

Notes.—1. The confirmatory test for copper is more delicate than the formation of a blue color with NH_4OH (P. 35). It should, therefore, be tried even when the NH_4OH solution is colorless. Cadmium is also precipitated by $K_4Fe(CN)_6$; but the precipitate is white, and does not prevent the pink color of the copper compound from being detected, provided only a small quantity of $K_4Fe(CN)_6$ is added; for the copper salt, owing to its smaller solubility, is first precipitated.

2. Nickel, like copper, givs a blue solution with excess of NH_4OH; but even if present it would giv a green, not a red, precipitate with $K_4Fe(CN)_6$.

Procedure 38.—*Detection of Cadmium.*—Treat the remainder of the NH_4OH solution (P. 35) with KCN solution (see Note 1), adding only a few drops if the solution is colorless, but enough to decolorize it if it is blue, and pass in H_2S gas for about half a minute. (Immediate yellow precipitate, presence of CADMIUM.)

Notes.—*1. In working with KCN bear in mind that it is extremely poisonous. Take care not to get it on the hands; also not to breathe its fumes, especially when a solution containing it is acidified.*

2. By the addition of KCN the copper salt is reduced from the cupric to the cuprous state and then combines with the excess of KCN to form the complex salt $K^+{}_3Cu(CN)_4^{\equiv}$ (potassium cuprocyanide). This result is due to the fact that cupric cyanide tends to decompose spontaneously into cuprous cyanide

(CuCN) and cyanogen $(CN)_2$, and that this reaction takes place completely in KCN solution, owing to removal of the CuCN by combination with the excess of KCN. In the presence of NH_4OH the cyanogen is not evolved as a gas, but reacts with it, forming cyanate (NH_4CNO) and cyanide and other more complex products. The fact that neither CuS nor Cu_2S is precipitated from this solution by an alkaline sulfide shows that neither the Cu^{++} nor Cu^+ concentration is sufficient to cause the value of the product $(Cu^{++}) \times (S^{=})$ or $(Cu^+)^2 \times (S^{=})$ to attain that prevailing in solutions saturated with CuS or Cu_2S. The extremely small Cu^+ concentration is due to the very slight ionization tendency of the complex anion $Cu(CN)_4^{\equiv}$; thus it has been estimated that in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cu^+ ion is about 10^{26}.

3. The cadmium ammonia salt is also converted by KCN into a complex cyanide, namely, $K^+_2Cd(CN)_4^{=}$ (potassium cadmicyanide), since its complex anion has a much smaller ionization tendency than the cation $Cd(NH_3)_4^{++}$; thus in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cd^{++} ion is about 10^{17}. Yet this complex anion is sufficiently dissociated into Cd^{++} to cause the solution to become supersaturated with CdS when an alkaline sulfide is added.

4. The presence of cadmium is shown by the immediate formation of a yellow precipitate by the H_2S, but not by a yellow coloration of the solution nor by the separation of a precipitate upon standing. For, when much copper is present and the solution is saturated with H_2S and allowed to stand, the solution soon becomes of a deep yellow color and an orange-red crystalline precipitate may later separate from it, owing to the fact that the orange-red compound $(CSNH_2)_2$ is formed by union of the H_2S with the $(CN)_2$ set free by the reduction of the $Cu(CN)_2$.

5. A very small black precipitate (which may be due to HgS or PbS) may sometimes be produced in the final test for cadmium with H_2S; but, provided the analysis has been properly conducted, not in sufficient quantity to prevent the yellow color of 1 or 2 mg. of CdS from being seen. In case a black precipitate is produced, and thus prevents a positiv conclusion as to the presence or absence of a little cadmium, the precipitate may be treated, in order to eliminate the black sulfide, as follows: Filter out the precipitate, wash it thoroly, rinse it into a casserole with about 15 cc. of 1.2-normal H_2SO_4, cover the casserole, boil the mixture gently for 5 minutes, filter it, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for 5–10 minutes. A yellow precipitate of CdS will then be obtained if cadmium is present.

ANALYSIS OF THE TIN-GROUP.

TABLE VI.—ANALYSIS OF THE TIN-GROUP.

<table>
<tr><td colspan="3">PRECIPITATE FROM AMMONIUM SULFIDE SOLUTION: As_2S_5, Sb_2S_5, SnS_2.
Heat with 10 cc. 12-normal HCl (P. 41).</td></tr>
<tr><td colspan="2">Solution: $SbCl_3$, $SnCl_4$. *Dilute to 55 cc., heat, and pass in H_2S (P. 44).*</td><td>Residue: As_2S_5. *Dissolve in HCl and $KClO_3$ (P. 42).*</td></tr>
<tr><td>Orange precipitate: Sb_2S_3. *Dissolve in HCl, add Sn and Pt (P. 45).*</td><td>Solution: $SnCl_4$. *Cool, dilute, pass in H_2S (P. 46).*</td><td>Solution: H_3AsO_4. *Add NH_4OH, NH_4Cl, and $MgCl_2$ (P. 43).*</td></tr>
<tr><td>Black deposit: Sb.? *Treat with NaOCl.*</td><td>Yellow precipitate: SnS_2. *Evaporate without filtering, add Pb, boil (P. 46.)*</td><td>White precipitate: $MgNH_4AsO_4$. *Dissolve in HCl, add H_2S (P. 43).*</td></tr>
<tr><td>Black deposit: Sb.</td><td>Solution: $SnCl_2$. *Add $HgCl_2$ (P. 46).*</td><td>Yellow precipitate: As_2S_5, As_2S_3, and S.</td></tr>
<tr><td></td><td>White precipitate: Hg_2Cl_2.</td><td></td></tr>
</table>

Procedure 41.—*Treatment of the Sulfides with Strong Hydrochloric Acid.*—Transfer the precipitated sulfides dried by suction (P. 23) to a test-tube, add from a small graduate exactly 10 cc. 12-normal HCl, place the test-tube in a small beaker of water, heat the water till the contents of the tube begin to boil, and then keep the water for ten minutes at a temperature which causes only slight bubbling in the tube, stirring its contents from time to time. Add 3 cc. water, and filter with the aid of suction. Remove the filtrate, and treat it by P. 44. Wash the residue with 6-normal HCl, and treat it by P. 42.

Notes.—1. If a much weaker HCl solution than the acid of 12-normal concentration is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much Sb_2S_5 will be left undissolved. Even with the strong acid some Sb_2S_5 may remain undissolved, especially when a large quantity is present, in which case the residue if small in amount will have an orange color. This small quantity of Sb_2S_5 would be only very slowly removed by further treatments with HCl; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of Sb_2S_5 is originally present, a large proportion of it is extracted, so that it will not escape detection. Sb_2S_5 dissolves with formation of $SbCl_3$, the element being reduced from the antimonic state by the H_2S with liberation of sulfur; SnS_2 dissolves with formation of $SnCl_4$.

2. If the solution be heated so that only slight bubbling occurs during the treatment with HCl, the amount of As_2S_5 which dissolves in ten minutes is insignificant. But this is no longer true if the solution be allowed to boil rapidly; for the boiling expels from the solution the H_2S liberated from the other sulfides or by slight decomposition of the As_2S_5 itself, and thus enables the decomposition of the latter to proceed further.

3. As_2S_3 is more rapidly dissolved by HCl than is As_2S_5. If the former can be present in the precipitate (which can be the case only when ammonium monosulfide was used for separating the copper and tin groups), the procedure should be modified by saturating with H_2S gas the cold concentrated HCl with which the sulfides are treated, and by passing a slow current of H_2S gas through the mixture during the heating. Under these conditions scarcely any As_2S_3 dissolves.

4. About 3 cc. water are added to the HCl solution to enable it to be filtered. If more is added and the H_2S has not all been expelled from the solution, a precipitate of Sb_2S_3 may separate. If this happens after the filtration, it does, of course, no harm.

5. Care must be taken to follow closely the directions in regard to the quantity of HCl used and to avoid any loss of the solution in the filtration; for the subsequent separation of antimony and tin (P. 44) depends upon a proper concentration of the acid.

6. The greater part of any CuS and HgS present will be dissolved by the HCl, and will be precipitated later with the Sb_2S_3 (P. 44). A little remains with the As_2S_5, but this does not interfere with the tests for arsenic.

Procedure 42.—*Detection of Arsenic.*—Warm the residue from the HCl treatment (P. 41) with 5–10 cc. 6–normal HCl, adding solid $KClO_3$ 0.1 g. at a time until the reaction is complete; filter off the sulfur, and evaporate the solution to about 2 cc. Add NH_4OH gradually until the solution after shaking smells of it; cool, filter off and reject any precipitate. Add to the filtrate in a test-tube about one-third its volume of 15–normal NH_4OH and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test-tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of ARSENIC.) Collect the precipitate on a filter and wash it once with 6–normal NH_4OH. (Precipitate, P. 43; filtrate, reject.)

Notes.—1. The main reaction between $KClO_3$ and concentrated HCl is the formation of Cl_2; the yellow color results from the formation of a small proportion of chlorine dioxide, ClO_2.

2. As_2S_5, tho only very slowly dissolved by HCl alone, is dissolved rapidly by it in the presence of Cl_2, because of the destruction by oxidation of the sulfide-ion and of the H_2S formed from it. The same principles are involved as in the action of HNO_3 on sulfides (see P. 31, Note 2). It is dissolved with formation of H_3AsO_4; the proportion of $AsCl_5$ that exists even in a strong

HCl solution is extremely small. When, as here, arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitativ analysis.

3. A white precipitate produced on adding NH_4OH may arise from the presence of mercury. The NH_4OH solution may contain not only arsenic, but also the small quantities of copper (if ammonium polysulfide was used), antimony, and stannic tin that were not dissolved out of the sulfide precipitate by HCl.

4. The test for arsenic depends on the formation of magnesium ammonium arsenate, $Mg(NH_4)AsO_4$. This salt is somewhat soluble even in cold water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into NH_4OH and $Mg^{++}HAsO_4^{-}$), the precipitate is much more soluble in water than in a strong NH_4OH solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating the solution and adding NH_4OH. Provided these precautions are taken and the total volume of the final solution does not exceed 5 cc., the presence of 0.5 mg. of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the $MgNH_4AsO_4$ precipitate.

5. The magnesium ammonium chloride reagent contains $MgCl_2$ and NH_4Cl. The presence of the latter salt, by reducing the OH^- concentration, prevents the precipitation of $Mg(OH)_2$ by NH_4OH.

Procedure 43.—*Confirmatory Test for Arsenic.*—Dissolve the $MgCl_2.NH_4Cl$ precipitate (P. 42) by pouring 5–10 cc. HCl through the filter, saturate the solution with H_2S, heat it nearly to boiling, and pass in H_2S again for 5 minutes. (White precipitate turning yellow, presence of ARSENIC.)

Notes.—1. The slow formation of a pale yellow precipitate with H_2S is a characteristic test for H_3AsO_4. The precipitate is a mixture of As_2S_5, As_2S_3, and sulfur; the proportion of As_2S_5 being smaller, the higher the temperature at which the precipitation takes place and the smaller the concentration of the HCl.

2. A considerable amount of H_2S is absorbed by a cold H_3AsO_4 solution before any precipitate appears. This is due to the conversion of a part of the H_3AsO_4 into H_3AsO_3S, which then decomposes slowly, giving H_3AsO_3 and sulfur. This last decomposition is accelerated by increasing the H^+ concentration and by raising the temperature. The H_3AsO_3 formed reacts at once with H_2S, and As_2S_3 is precipitated. The reactions taking place are:

$$\begin{aligned} H_3AsO_4 + H_2S &= H_3AsO_3S + H_2O, \\ H_3AsO_3S &= H_3AsO_3 + S, \\ 2H_3AsO_3 + 3H_2S &= As_2S_3 + 6H_2O, \end{aligned}$$

which together giv the resultant reaction,

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

The rate of this reaction depends upon the rate of the slowest of the separate reactions—the decomposition of the H_3AsO_3S—and on the quantity of this substance which has been produced by the first reaction. This quantity seems to be determined by the equilibrium-conditions of the first reaction rather than by its rate; for it is larger when the solution is saturated in the cold with H_2S, doubtless owing to the greater solubility of the H_2S in the cold solution. This explains why it is advantageous to saturate the solution with H_2S first in the cold. Having formed in this way as large a proportion of H_3AsO_3S as possible, the solution is then heated in order to cause decomposition of this substance according to the second reaction.

3. As_2S_5 results from an independent reaction, taking place slowly, as follows:

$$2H_3AsO_4+5H_2S=As_2S_5+8H_2O.$$

The fact that it is the main product of the action of the H_2S when the solution is cold and concentrated in HCl is doubtless due to the conversion of more of the H_3AsO_4 into $AsCl_5$ under these conditions (which are those least favorable to hydrolysis) and to the partial ionization of the $AsCl_5$ into As^{+++++} and Cl^- ions.

Procedure 44.—*Separation of Antimony and Tin.*—Dilute the solution from the HCl treatment of the sulfides (P. 41) with water to a volume of 55 cc., transfer it to a small flask placed in a 400-cc. beaker of water, heat the water to boiling, and pass into the solution a moderate current of H_2S gas for 8–10 minutes but not longer, keeping the water in the beaker gently boiling. (Orange-red precipitate, presence of ANTIMONY.) Filter while hot, and wash the precipitate with hot water. (Precipitate, P. 45; filtrate, P. 46.)

Notes.—1. By following carefully the directions given in P. 41 and in this procedure, a good separation of antimony and tin may be obtained; thus, when only 1 mg. of antimony is present it is precipitated, while even 500 mg. of (stannic) tin giv no precipitate. If, however, the HCl solution be more concentrated, a small quantity of antimony will escape detection. On the other hand, if the HCl solution be more dilute, or if it be not kept hot, some SnS_2 may precipitate when a large amount of tin is present. When SnS_2 is mixed with a little Sb_2S_3 a brown precipitate results.

2. If mercury or copper be present in the substance and ammonium polysulfide has been used in separating the copper and tin groups, HgS or CuS may be precipitated at this point as a gray or black precipitate.

Procedure 45.—*Confirmatory Test for Antimony.*—Dissolve the H_2S precipitate (P. 44) in a little 12-normal HCl in a small casserole, and evaporate the solution to about 1 cc. Cool, introduce beneath the solution a strip of platinum foil, and place upon the platinum a layer of granulated tin. After several minutes wash the platinum foil carefully with water, and immerse it in NaOCl solution. (Black deposit on the platinum undissolved by NaOCl, presence of ANTIMONY.)

Notes.—1. Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from the gray deposit of mercury or the reddish one of copper by its coal-black color. Tin is used, rather than zinc, in precipitating the antimony, since zinc would also precipitate tin from the solution.

2. By the contact of the platinum with the tin a voltaic cell is formed, with the result that the hydrogen is liberated on the surface of the platinum, instead of on that of the tin, as it would be if tin alone were used. This has the advantages of accelerating the action of the acid on the tin, and of causing the antimony to deposit on the platinum, where it can be more readily seen.

3. The treatment with NaOCl serves to prove that the black precipitate does not consist of arsenic; for this element is readily dissolved by it, while antimony, copper, or mercury is not. Since, however, 5–10 mg. of arsenic must be present before the treatment with tin would giv a deposit on the platinum, an arsenic deposit is not likely to be obtained in a properly conducted analysis.

4. The quantity of antimony present can usually be better estimated from the size of the H_2S precipitate than from the appearance of the black deposit on the platinum.

Procedure 46.—*Detection of Tin.*—Cool the filtrate from the H_2S precipitate (P. 44), dilute it with 25 cc. water, saturate it with H_2S, cork the flask, and let it stand for 10 minutes. (Yellow precipitate, presence of TIN.)

Confirmatory Test for Tin.—If H_2S has produced a precipitate, evaporate the mixture without filtering to 2–3 cc., pour it into a small conical flask, add 10 cc. water and 10 g. of finely granulated lead, cover the flask with a small watch-glass, and boil slowly for 5 to 10 minutes. Pour the hot solution through a filter into 10 cc. 0.2 normal $HgCl_2$ solution. If there is a precipitate, heat the mixture to boiling. (White precipitate, presence of TIN.)

Notes.—1. The solution is precipitated with H_2S in the cold, because a small quantity of SnS_2 would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test. When only a small quantity (0.5–2 mg.) of tin is present, the precipitate of SnS_2 produces in the solution a yellowish translucent turbidity, which is readily distinguishable from the trace of finely divided sulfur which may separate.

2. With respect to the confirmatory test the following points deserve mention. The precipitate of SnS_2 is not filtered off but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. Since $SnCl_2$ oxidizes rapidly in the air, the solution in HCl is immediately added to the $HgCl_2$ solution. The mixture is finally heated to boiling to make sure that the precipitate is not $PbCl_2$.

PRECIPITATION AND SEPARATION OF THE ALUMINUM AND IRON GROUPS.

TABLE VII.—PRECIPITATION AND SEPARATION OF THE ALUMINUM AND IRON GROUPS.

<table>
<tr><td colspan="3">FILTRATE FROM THE HYDROGEN SULFIDE PRECIPITATE.
Add NH_4OH in excess (P. 51).</td></tr>
<tr><td colspan="3">Precipitate*: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_{2-3}$; also $Mn(OH)_2$ after exposure to air
Solution: Salts of $Zn(NH_3)_4$, $Co(NH_3)_4$, $Ni(NH_3)_4$, Mn, Ba, Sr, Ca, Mg, K, and Na
Add $(NH_4)_2S$ and filter (P. 51).</td></tr>
<tr><td colspan="2">Precipitate*: $Al(OH)_3$, $Cr(OH)_3$, FeS, ZnS, MnS, CoS, NiS.
Dissolve in HCl and HNO_3, add NaOH (P. 52).</td><td rowspan="3">Filtrate: Salts of Ba, Sr, Ca, Mg, K, Na.</td></tr>
<tr><td colspan="2">Precipitate*: $Fe(OH)_3$, $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$.
Solution: $NaAlO_2$, $NaCrO_2$, Na_2ZnO_2.
Add Na_2O_2 and filter (P. 52).</td></tr>
<tr><td>Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2.
See Table VIII.</td><td>Precipitate*: $Fe(OH)_3$, $MnO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$.
See Table IX.</td></tr>
</table>

*When phosphate is present in the solution, these precipitates may contain the phosphates of the elements otherwise precipitated as hydroxides, and also the phosphates of barium, strontium, calcium, and magnesium.

Procedure 51.—*Precipitation of the Aluminum and Iron Groups.*—Boil the filtrate from the H_2S precipitate (P. 21) till the H_2S is expelled. Add to it 10–15 cc. NH_4OH, shake, and note whether there is a precipitate. Add ammonium monosulfide slowly (or, in case nickel seems to be present, pass in H_2S) until, after shaking, the vapors in the flask blacken moist $PbAc_2$ paper. Heat the mixture nearly to boiling, shake it, and let it stand 2 or 3 minutes. (Precipitate, presence of ALUMINUM-GROUP or IRON-GROUP or of ALKALINE-EARTH PHOSPHATE.) Filter, and wash the precipitate, first with water containing about 1% of the $(NH_4)_2S$ reagent, and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch-glass. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds (or, in case it is dark colored, until it becomes colorless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 81.)

Notes.—1. The H_2S is boiled out and the effect of the addition of NH_4OH alone is noted because it often givs a useful indication as to what elements are present. To save time the expulsion of the H_2S may be omitted when this indication is considered unimportant. Only a slight excess of ammonium monosulfide is used, in order to prevent as far as possible dissolving the NiS. By passing H_2S into the ammoniacal solution, instead of adding $(NH_4)_2S$, the dissolving of NiS is entirely prevented; therefore, tho the operation takes a little longer, the use of H_2S is to be preferred when nickel is likely to be present. The mixture is shaken in order to coagulate the precipitate and make it filter more readily. Heating also promotes the coagulation of the precipitate; heat is therefore applied when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black color of the filtrate. Finally, it is directed to wash with water containing a little $(NH_4)_2S$ and to keep the filter covered, in order that some excess of $(NH_4)_2S$ may always be present; for, if the $(NH_4)_2S$ adhering to the precipitate is removed by oxidation or by volatilization (as H_2S and NH_3), the sulfides are oxidized to soluble sulfates by the air.

2. Under the conditions of the procedure, which provides for a small excess of NH_4OH in the presence of ammonium salt, aluminum, chromium, and iron are completely precipitated. $Al(OH)_3$ is white; $Cr(OH)_3$, grayish green. The color of the precipitated iron hydroxide varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish brown one, while mixtures of them yield green or black precipitates; in the alkaline mixture the precipitate is rapidly oxidized by the oxygen of the air and undergoes corresponding changes in color. Under the conditions of the procedure manganese is not precipitated as $Mn(OH)_2$; but in the alkaline solution the manganous salt is rapidly oxidized by the air with the formation of a brown precipitate consisting of $Mn(OH)_3$ and MnO_3H_2 (a hydrate of MnO_2). Zinc, nickel, and the alkaline-earth elements remain in solution; nickel yielding a blue solution. Cobalt also remains dissolved (yielding a pink solution), unless the quantity present is large, in which case a blue precipitate may separate; owing to oxidation the solution rapidly changes to a dark orange, and the precipitate to a bright green color. When much chromium is present, zinc and magnesium may be completely precipitated in combination with it. If a much larger excess of NH_4OH is employed than is directed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

3. The presence of ammonium salts in the solution serves to prevent the precipitation of $Mg(OH)_2$, and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

4. The influence of an excess of the NH_4OH and of the presence of ammonium salt on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type MO_2H_2, may be precipitated, it is necessary that the product $(M^{++})\times(OH^-)^2$ of the concentrations of the ions M^{++} and OH^- in the solution under consideration attain the saturation-value of that product. This saturation-value varies, of course, with the nature of the hydroxide; but for all the elements of the iron-group and for magnesium, it is so small that

even in a solution containing in 50 cc. only 1 mg. of the element and a slight excess of NH_4OH, the product $(M^{++}) \times (OH^-)^2$ exceeds it, and precipitation results. When, however much ammonium salt is also present, this greatly reduces, in virtue of the common-ion effect, the ionization of the NH_4OH and therefore the OH^- concentration in the solution, so that now for certain elements the product $(M^{++}) \times (OH^-)^2$ does not reach the saturation-value, even when (M^{++}) is moderately large (say 500 mg. in 50 cc.). This is true of magnesium and manganese; but in the cases of the trivalent elements, aluminum, chromium, and ferric iron, the solubility of the hydroxides in water is so slight that even in ammonium salt solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cation M^{++}, forming complex cations of the types $M(NH_3)_2^{++}$ and $M(NH_3)_4^{++}$, thereby removing the simple cation from the solution and making it necessary for more of the hydroxide to dissolve in order to bring back the value of $(M^{++}) \times (OH^-)^2$ to the saturation-value. In such a case the presence of ammonium salt increases the solubility still further, since it greatly decreases the value of (OH^-), owing to the common-ion effect on the ionization of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second kind of effect is exhibited in the case of AlO_3H_3. This hydroxide is another example of an amphoteric substance; for it behaves both as a base and as an acid in consequence of its being appreciably ionized both into OH^- and Al^{+++} and into H^+ and $AlO_3H_2^-$ (or into H^+, AlO_2^-, and H_2O). With the H^+ arising from the latter form of ionization the OH^- coming from the excess of NH_4OH combines to form H_2O, so as to satisfy the mass-action expression for the ionization of water, $(H^+) \times (OH^-) =$ a constant (which has the very small value 10^{-14} at 25°). This causes more AlO_3H_3 to dissolve until the product $(AlO_2^-) \times (H^+)$ again attains its saturation-value. This shows that the quantity of aluminum dissolved increases with the OH^- concentration in the solution, and that therefore it would be much greater in a solution of a largely ionized base like NaOH than in that of a slightly ionized base like NH_4OH. It also shows that the presence of ammonium salts tends to neutralize the solvent action of an excess of NH_4OH, since they decrease the OH^- concentration in its solution.

5. It follows from the statements in the preceding notes that, if NH_4OH produces no precipitate, it proves the absence of as much as 1 mg. of aluminum and iron; also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be heated and shaken and allowed to stand 2 or 3 minutes, in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

6. When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely, precipitated by NH_4OH

The reasons for this are as follows. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates and of free phosphoric acid. Upon the addition of an excess of NH_4OH to such a solution these acid compounds are converted into the normal phosphates, and these are reprecipitated. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline-earth elements in the analysis of the NH_4OH precipitate. They are, however, not necessarily found in that precipitate; for, when other elements, like iron and aluminum, which form much less soluble phosphates, are also present, these may combine with all the phosphate-ion present, thus leaving the alkaline-earth elements in solution.

7. The presence of any other acidic constituent which forms with the alkaline-earth elements salts soluble in dilute acids, but insoluble in ammonia, may also cause their precipitation at this point. Fluoride is the only common inorganic constituent of this kind, and it will ordinarily have been removed in the evaporation with acids in the preparation of the solution.

8. $(NH_4)_2S$ precipitates ZnS, MnS, NiS, and CoS, and converts $Fe(OH)_2$ into FeS, and $Fe(OH)_3$ into Fe_2S_3. The hydroxides of aluminum and chromium are not affected by the $(NH_4)_2S$.

9. The sulfides of iron, nickel, and cobalt are black; ZnS is white; and MnS is flesh-colored, but turns brown on standing in the air, owing to oxidation to $Mn(OH)_3$ and MnO_3H_2.

10. When nickel is present alone or when it forms a large proportion of the $(NH_4)_2S$ precipitate, several milligrams of it usually pass into the filtrate, giving it a brown or black color; and some NiS also passes through the filter with the wash-water. In this case it is useless to try to remove the NiS by filtering again, but it can be coagulated by boiling for several minutes. The brown solution is formed only in the presence of ammonium polysulfide. Its formation can, as stated above, be avoided altogether by passing H_2S into the NH_4OH solution, instead of adding the ammonium monosulfide reagent, which after exposure to the air always contains some polysulfide. The nature of the brown solution is not known.

Procedure 52.—*Separation of the Aluminum-Group from the Iron-Group.*—Transfer the $(NH_4)_2S$ precipitate (P. 51), with the filter if necessary, to a casserole; add 5–20 cc. HCl, stir for a minute or two in the cold, and then boil the mixture for 2 or 3 minutes; if a black residue still remains, add a few drops of HNO_3 and boil again. Add 5–10 cc. water, filter off the sulfur residue, and evaporate the filtrate almost to dryness to remove the excess of acid. (See Note 2, P. 12.)

Dilute the solution to 10 or 20 cc., and add to it NaOH solution, a few drops at a time, till the solution turns red litmus paper blue, adding 10–20 cc. more water if so large a precipitate separates that the mixture becomes thick with it. Place the casserole in a dish of cold water, and add 0.5–2.0 cc. Na_2O_2 powder in small portions with constant stirring. (See Notes 5 and 9.) Then add 5 cc. 3-normal Na_2CO_3 solution; boil for 2 or 3 minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction, and wash with hot water. (Precipitate, P. 61; filtrate, P. 53.)

Notes.—1. All the hydroxides and all the sulfides, except NiS and CoS, usually dissolve readily in cold HCl. If, therefore, there is considerable black residue after adding the HCl, it shows the presence of nickel or cobalt; a very small black residue may, however, be due to FeS enclosed within sulfur. The fact that there is no such dark-colored residue does not, however, prove that nickel and cobalt are entirely absent; for a considerable quantity of them (even 5 mg.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

2. The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt, but also because much more free sulfur and sulfate would be formed by oxidation if HNO_3 or *aqua regia* were used at the start. (The presence of much sulfate in the solution interferes with the subsequent test for chromate.) If NiS or CoS is present in the residue, HNO_3 must, however, be subsequently added, to ensure the solution of these sulfides.

3. By NaOH, iron, manganese, nickel, and cobalt are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, and zinc remain in solution or dissolve when a sufficient excess is added. The solubility of the last three elements is due to the fact that their hydroxides are amphoteric substances which form with the NaOH soluble aluminate ($NaAlO_2$), chromite ($NaCrO_2$), and zincate (Na_2ZnO_2), respectivly. When zinc and chromium are simultaneously present they are precipitated in the form of a double compound ($ZnCr_2O_4$). Chromium would also be completely precipitated, owing to hydrolysis of the chromite and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. $Mn(OH)_2$ is white, but rapidly turns brown, owing to oxidation to $Mn(OH)_3$; $Ni(OH)_2$ is light green; $Co(OH)_2$ is pink, but from cold cobaltous salt solutions a blue basic salt is first precipitated. If a large excess of NaOH be added, a little $Co(OH)_2$ dissolves, yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided, since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of Na_2O_2.

4. By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, and $Co(OH)_2$ to black $Co(OH)_3$, all of which are insoluble in excess of NaOH. Chromium, which after the addition of cold NaOH is present as soluble sodium chromite ($NaCrO_2$), is converted by Na_2O_2 into chromate (Na_2CrO_4). This remains in solution together with the zinc, which is still present as zincate.

5. Even a cold solution of Na_2O_2 decomposes slowly with evolution of oxygen, and this decomposition takes place with explosiv violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. It is best to transfer a little of it from the can in which it comes in trade directly (without using paper) to a dry 10-cc. graduate, and then to sprinkle it into the solution with constant stirring. A steady evolution of gas after

the mixture has been well stirred is an indication that sufficient peroxide has been added. When much chromium is present, it should be added till the green precipitate disappears and the liquid assumes a dark yellow color. The solution is diluted before filtering in order to avoid the disintegration of the filter-paper. It is also often advantageous to support the filter by folding it together with a small hardened filter.

6. This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. As much as 5 mg. of this element is almost completely carried down in the precipitate when much iron, nickel, or cobalt is present; and as much as 20 mg. of it may be completely precipitated when much manganese is present. Provision is therefore made for the detection of zinc in the precipitate.

7. The Na_2CO_3 is added to ensure the complete precipitation of magnesium, calcium, strontium, and barium, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, tho insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to nearly complete conversion of the zinc-ion into zincate-ion ($ZnO_2^{=}$). The Na_2CO_3 also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline-earth elements are known to be absent.

8. Phosphate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the basic elements present. (See P. 51, Note 6.) Its presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum and zinc phosphates. This is due to the fact that the cations of these elements (Al^{+++}, Zn^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their conversion by the OH^- into anions (AlO_2^-, $ZnO_2^{=}$).

9. In actual analyses (except in those made for practis) it is advantageous to omit the addition of the NaOH and to use in place of it a somewhat larger quantity (0.5 cc. more) of the Na_2O_2 powder; for even the best commercial NaOH is apt to contain impurities, such as silicate or sulfate, which interfere with the subsequent detection of aluminum or chromium.

ANALYSIS OF THE ALUMINUM-GROUP.

TABLE VIII.—ANALYSIS OF THE ALUMINUM-GROUP.

<table>
<tr><td colspan="3">FILTRATE FROM THE SODIUM HYDROXIDE AND PEROXIDE TREATMENT: Na_2ZnO_2, $NaAlO_2$, Na_2CrO_4. *Acidify with* HNO_3, *add* NH_4OH *(P. 53).*</td></tr>
<tr><td rowspan="2">Precipitate: $Al(OH)_3$. *Dissolve in* HNO_3, *add* $Co(NO_3)_2$, *evaporate, ignite (P. 54).*</td><td colspan="2">Filtrate. *Add HAc and* $BaCl_2$ *(P. 55).*</td></tr>
<tr><td>Precipitate: $BaCrO_4$. *Dissolve in HCl and* H_2SO_3, *evaporate (P. 56).*</td><td>Filtrate: Zinc salt. *Pass in* H_2S *(P. 57).*</td></tr>
<tr><td rowspan="2">Blue residue: $Co(AlO_2)_2$.</td><td rowspan="2">Green color: $CrCl_3$.</td><td>White precipitate: ZnS. *Dissolve in* HNO_3, *add* $Co(NO_3)_2$ *and* Na_2CO_3, *ignite (P. 57).*</td></tr>
<tr><td>Green residue: $CoZnO_2$.</td></tr>
</table>

Procedure 53.—*Separation of Aluminum from Chromium and Zinc.*—Acidify the alkaline solution (P. 52) with 16-normal HNO_3, avoiding a large excess; add NH_4OH until the mixture after shaking smells of it, and then add 2–3 cc. more. (White flocculent precipitate, presence of ALUMINUM.) Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroly with hot water. (Precipitate, P. 54; filtrate, P. 55.)

Notes.—1. The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of the complex cation $Zn(NH_3)_4^{++}$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4^+AlO_2^-$. The zinc dissolves even when carbonate or phosphate is present

2. Since aluminum and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, a blank test for these impurities should be made whenever new reagents are employed for the first time, by treating 20 cc. of the NaOH reagent, or 2 g. of Na_2O_2 added to 20 cc. water, by P. 53 and comparing the NH_4OH precipitate with that obtained in the actual analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57. The NaOH reagent should also be tested for sulfate by acidifying it with HCl and adding $BaCl_2$, since the presence of much sulfate obscures the test for chromium in P. 55.

Procedure 54.—*Confirmatory Test for Aluminum.*—Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 cc. HNO_3. To the solution add from a dropper half as many drops of a $Co(NO_3)_2$ solution containing 1% Co as the number of milligrams of aluminum estimated to be present in the solution. Evaporate the solution almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter paper. Make a small roll of the paper, wind a platinum wire around it in the form of a spiral, and heat the paper in a flame till the carbon is burnt off. (Blue residue, presence of ALUMINUM.)

Notes.—1. A confirmatory test for aluminum should always be tried when the NH_4OH precipitate is small; for the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and silicon showing a similar behavior). It is especially necessary to guard against mistaking SiO_3H_2 for $Al(OH)_3$; for the former substance, if not entirely removed in the process of preparing the solution, may appear at this point.

2. The confirmatory test with $Co(NO_3)_2$ depends upon the formation of a blue substance, whose formula is not definitely known; but it is doubtless a compound of the two oxides CoO and Al_2O_3, and is probably cobalt aluminate, $Co(AlO_2)_2$. It enables 0.5 mg. Al to be detected, or even 0.2 mg. after a little practis. No other element givs a blue color to the ash. It is essential to have the aluminum present in excess; for otherwise the blue color is obscured by the black oxide of cobalt. Moreover, when sodium or potassium salts are present, the ash fuses together and the test is unsatisfactory. For this reason the sodium salts present should be completely washed out of the NH_4OH precipitate before dissolving it in HNO_3.

Procedure 55.—*Detection of Chromium.*—To the NH_4OH solution (P. 53) add HAc, 1 cc. at a time, till the solution reddens blue litmus paper.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 cc. $BaCl_2$ solution, and heat the mixture to boiling. (Yellow precipitate, presence of CHROMIUM.) Filter, and wash the precipitate. (Precipitate, P. 56; filtrate, P. 57.)

Notes.—1. The presence of less than 0.5 mg. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow; and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration. In doubtful cases the color of the solution should be compared with that of water. The color-test is, of course, not delicate by artificial light.

2. Since some sulfate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow color of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If a large quantity of sulfate is present, not only may the yellow color of a little $BaCrO_4$ be obscured, but the confirmatory test described in P. 56 may fail owing to the imperfect extraction of the $BaCrO_4$ from the $BaSO_4$ by the acid. For this reason care must be taken not to use in P. 52 reagents containing much sulfate.

Procedure 56.—*Confirmatory Test for Chromium.*—Pour repeatedly through the filter (P. 55) a warm mixture of 3 cc. HCl and 10 cc. saturated SO_2 solution. Evaporate the filtrate in a casserole just to dryness, taking care not to over-heat the residue; and add a few drops of water. (Green coloration of the solution, presence of CHROMIUM.)

Note.—The green color of $CrCl_3$ is intense enough to enable less than 0.5 mg. of chromium in 1 cc. of solution to be detected. A yellow color may result from the action of the acids on the filter paper; but this color usually disappears on evaporating and dissolving the residue in water.

Procedure 57.—*Detection of Zinc.*—Warm the HAc solution (P. 55) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask, and allow it to stand for 5 or 10 minutes if no precipitate separates at once. (White flocculent precipitate, presence of ZINC.)

Confirmatory Test for Zinc.—Filter the H_2S precipitate through a double filter (made by folding two filters together), wash it with a little water, and pour a 5–10 cc. portion of HNO_3 repeatedly through the filter. To the filtrate add from a dropper one drop of a $Co(NO_3)_2$ solution containing 1% Co and as many more drops of the same solution as there were estimated to be centigrams of zinc in the H_2S precipitate. Evaporate the mixture in a casserole just to dryness to expel the acid, add 1 cc. Na_2CO_3 solution and 0.5 cc. more for each centigram of zinc estimated to be present. Evaporate to dryness, ignite gently by keeping the dish moving to and fro in a small flame until the purple color due to the cobalt disappears, and allow the casserole to cool. (Green color, presence of ZINC.) [If the ignited mass becomes black (owing to too strong heating), add a few drops HNO_3, evaporate just to dryness, add the same quantity of Na_2CO_3 solution as was added before, evaporate and ignite gently as before.]

Notes.—1. ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate; but since sulfur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

2. The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light-colored sulfide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small noncoagulating precipitate which may be sulfur results, or when, owing to the presence of a small quantity of other elements, the precipitate is dark-colored. In this test the use of an excess of $Co(NO_3)_2$ is avoided, since otherwise the black color of the CoO obscures the green color of the cobalt zincate ($CoZnO_2$).

ANALYSIS OF THE IRON-GROUP.

TABLE IX.—ANALYSIS OF THE IRON-GROUP.

<table>
<tr><td colspan="4">PRECIPITATE PRODUCED BY SODIUM HYDROXIDE AND PEROXIDE:
A. Phosphate absent: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, ZnO_2H_2*.
B. Phosphate present: Also $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $FePO_4$, $Ca_3(PO_4)_2$, etc.
Dissolve in HNO_3 and H_2O_2, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).</td></tr>
<tr><td rowspan="2">Precipitate:
MnO_2.
Add HNO_3 and bismuth dioxide (P. 62).</td><td colspan="3">Solution: *Test a portion for phosphate with $(NH_4)_2MoO_4$ (P. 63).*
A. Phosphate absent: *add NH_4OH (P. 64).*
B. Phosphate present: *add NH_4Ac and $FeCl_3$, dilute, boil (P. 65).*†</td></tr>
<tr><td rowspan="2">Precipitate:
A. $Fe(OH)_3$.
B. Basic ferric acetate and $FePO_4$.</td><td colspan="2">Filtrate: *add NH_4OH, pass in H_2S (P. 66).*</td></tr>
<tr><td>Purple color:
$HMnO_4$.</td><td>Precipitate: ZnS, CoS, NiS.
See Table X.</td><td>Filtrate:
A. NH_4 salts. *Reject.*
B. Ba, Ca, Sr, Mg.
Treat by P. 81.</td></tr>
</table>

* This precipitate may contain all the zinc when elements of the iron-group are present in large quantity.

† First testing a small portion of the solution for iron with KSCN.

Procedure 61.—*Precipitation of Manganese.*—Transfer the Na_2O_2 precipitate (P. 52) to a casserole, together with the filter if necessary, and add 5–15 cc. HNO_3. If there is still a residue, heat the mixture nearly to boiling and add 3% H_2O_2 solution, a few drops at a time, stirring after each addition, till the residue is dissolved. Filter to remove the paper, and evaporate the filtrate almost to dryness. Add 10 cc. 16-normal HNO_3 and about 1 g. of powdered $KClO_3$, and heat to boiling. (Black precipitate, presence of MANGANESE.)

If there is no precipitate, evaporate the solution almost to dryness, add 25 cc. water, and treat a part of the solution by P. 63 and the remainder by P. 64 or P. 65.

If there is a precipitate, add to the mixture 10 cc. 16-normal HNO_3, pour it into a 200 cc. conical flask, heat it to boiling, and add gradually (0.5 g. at a time) 3 g. powdered $KClO_3$. Grasp the neck of the flask with a strip of stiff paper, and keep the flask in motion over a small flame so that the mixture boils gently for one or two minutes. Make an asbestos filter by placing in a funnel enough glass-wool to form a wad 1 cm. high, tamping it down gently with the finger, and pouring through it a suspension of fine asbestos fibers in water, enough to form an asbestos layer about ½ cm. thick, applying suction at the same time. Filter the mixture with the aid of suction through this asbestos filter. Add to the filtrate 1 g. $KClO_3$. If more precipitate separates, boil the mixture gently for a minute or two, and then filter it through the same asbestos filter. Wash the precipitate two or three times with 16-normal HNO_3 which has previously been freed from oxides of nitrogen by warming it with a little $KClO_3$, and treat the precipitate by P. 62. Evaporate the filtrate to about 5 cc., but not further, dilute it with 25 cc. water, and treat a part of it by P. 63 and the remainder by P. 64 or P. 65.

Notes.—1. Pure concentrated HNO_3 does not dissolve hydrated MnO_2; but it may do so in the presence of filter-paper, whereby the HNO_3 is reduced to lower oxides. The action is rapid in the presence of H_2O_2; for the MnO_2 is thereby quickly reduced to $Mn(NO_3)_2$ with evolution of O_2.

2. By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized to hydrated MnO_2 with formation of chlorin dioxide (ClO_2), which escapes as a yellow gas.

3. The separation of manganese in this way from the other metals of this group is entirely satisfactory with the exception that a small quantity of iron (up to 1 mg.) may be completely carried down with a large quantity (500 mg.) of manganese.

Procedure 62.—*Confirmatory Test for Manganese.*—Pour through the filter containing the $KClO_3$ precipitate (P. 61) 5 cc. hot HNO_3 to which 4 or 5 drops of 3% H_2O_2 solution have been added. Collect the filtrate in a test-tube; cool it; add to it solid bismuth dioxide, 0.1 g. at a time, till some of the brown solid remains undissolved; and let the solid settle. (Purple solution, presence of MANGANESE.)

Notes.—1. This confirmatory test for manganese is usually superfluous, since the precipitation of MnO_2 by $HClO_3$ is highly characteristic.

2. An excess of bismuth dioxide must be added, since otherwise the manganese may be oxidized only to MnO_2.

3. Commercial bismuth dioxide, also often called sodium bismuthate, is a mixture of bismuth compounds which probably owes its oxidizing power to the presence of the dioxide BiO_2. When it is not available, PbO_2 may be substituted for it; but in that case the mixture must be boiled for 2 or 3 minutes.

Procedure 63.—*Test for Phosphate.*—Heat about one-tenth of the HNO_3 solution (P. 61) to boiling, and pour it into two or three times its volume of cold ammonium molybdate reagent. (Fine yellow precipitate, presence of PHOSPHATE.) If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65

Notes.—1. Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron can be separated from nickel and cobalt by NH_4OH (as in P. 64); but when considerable phosphate is present, alkaline-earth elements may also be present, and these would be partly or wholly precipitated by NH_4OH as phosphates. (See P. 51, Note 6.)

2. In order that the phosphate test may be delicate and that the precipitate may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warm. It is best, however, to heat only the solution to be tested, not the mixture of it with the reagent; for too much heating may cause solid MoO_3 to separate from the reagent. The precipitate produced by ammonium molybdate, $(NH_4)_2MoO_4$, is ammonium phosphomolybdate, a complex salt of the composition $(NH_4)_3PO_4(MoO_3)_{12}$.

Procedure 64.—*Precipitation of Iron in Absence of Phosphate.*—If phosphate is absent, make the HNO_3 solution (P. 61) strongly alkaline with NH_4OH, using an excess of 3–5 cc. (Dark red precipitate, presence of IRON.) Filter, and wash the precipitate thoroly. Treat the filtrate by P. 66. Dissolve the precipitate in HCl, warming if necessary; and to the solution add 3–5 cc. KCNS solution. (Red coloration, presence of IRON.)

Note.—This test may be made in the presence of much HCl, but not in the presence of much HNO_3; for HNO_3 acts on KCNS forming a red-colored compound. This test for iron is an extremely delicate one; and if only a faint color is obtained, the acids used in the process must be tested for iron. The red color is due to the formation by metathesis of ferric thiocyanate, $Fe(CNS)_3$, a slightly ionized substance.

Procedure 65.—*Detection of Iron and Removal of Phosphate when Present.*—If phosphate is present, test one-tenth of the HNO_3 solution (P. 61) for iron, by evaporating it just to dryness, adding 1–2 cc. 12-normal HCl, evaporating again just to dryness, dissolving the residue in 2 cc. HCl and 5 cc. water, and adding 5 cc. KCNS solution. (Red coloration, presence of IRON.) To the remainder of the solution add NH_4OH until the precipitate formed by the last drop does not redissolve on shaking. If, owing to the addition of too much NH_4OH, the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 15 cc. of a 3-normal solution of NH_4Ac, and, unless the mixture is already of a brownish-red color, add $FeCl_3$ solution, drop by drop, until such a color is produced. Add enough water to make the volume about 100 cc., boil in a 250 cc. flask for 5 minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 10 cc. more NH_4Ac solution to the filtrate, boil it again, and collect on a separate filter any further precipitate. Reject the precipitate. Make the filtrate alkaline with NH_4OH, and treat it by P. 66.

Notes.—1. With regard to the test for iron with KCNS and the necessity of removing the HNO_3 by the evaporation with HCl, see P. 64, Note.

2. This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron is completely precipitated in the form of a basic acetate; and that all the phosphate present combines with the iron when it is present in excess, and therefore then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent elements is much smaller than that of the phosphates of the bivalent elements.

3. If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and $FeCl_3$ is therefore added. This causes the precipitation of $FePO_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.

4. The solution is diluted to at least 100 cc., owing to the large volume of the precipitate; and it is heated in a capacious flask, owing to its tendency to boil over.

Procedure 66.—*Precipitation of Zinc, Nickel, and Cobalt.*—Into the ammoniacal solution (P. 64 or P. 65) pass H_2S gas until the mixture after shaking blackens $PbAc_2$ paper held above it. (Black precipitate, presence of NICKEL or COBALT.) Filter, wash the precipitate with water containing a very little $(NH_4)_2S$, and treat it by P. 67. Treat the filtrate by P. 81–89 if phosphate or much chromium was found present (in P. 63 or P. 55); otherwise, reject it.

Notes.—1. In precipitating NiS, the use of H_2S has the advantage that the nickel is all thrown down at once, while with $(NH_4)_2S$ some of it usually remains in the solution, giving it a dark brown color. If $(NH_4)_2S$ be used, the filtrate must be boiled to throw down the unprecipitated nickel, as described in P. 51.

2. The filtrate must be treated by the procedures for detecting alkaline-earth elements when phosphate has been found to be present, since the whole quantity of these elements present in the substance may then be contained in this filtrate, for the reasons stated in Note 6, P. 51, and Note 2, P. 65. The filtrate should also be so treated when much chromium is present, since all the magnesium present may have been carried down with it in the original $(NH_4)_2S$ precipitate.

TABLE X.—SEPARATION OF ZINC, NICKEL, AND COBALT.

<table>
<tr><td colspan="3">HYDROGEN SULPHIDE PRECIPITATE: ZnS, NiS, CoS.
<i>Treat with cold dilute HCl (P. 67).</i></td></tr>
<tr><td colspan="2">Solution: $ZnCl_2$, $NiCl_2$*, $CoCl_2$*
<i>Add NaOH and Na_2O_2 (P. 67).</i></td><td rowspan="2">Residue: NiS, CoS.
<i>Dissolve in HCl and HNO_3, evaporate (P. 68).</i></td></tr>
<tr><td>Filtrate: Na_2ZnO_2.
<i>Add HAc and H_2S.</i></td><td>Precipitate: $Ni(OH)_2$, $Co(OH)_3$.
<i>Add HCl, evaporate (P. 68).</i></td></tr>
<tr><td>White precipitate: ZnS.</td><td colspan="2">Residue: $NiCl_2$, $CoCl_2$. <i>Add HCl and ether (P. 68).</i></td></tr>
<tr><td></td><td>Yellow residue: $NiCl_2$.
<i>Dissolve in water, add tartaric acid, NaOH, and H_2S (P. 69).</i></td><td>Blue solution: $CoCl_2$.
<i>Evaporate, add HAc and KNO_2 (P. 70).</i></td></tr>
<tr><td></td><td>Brown coloration: presence of nickel.</td><td>Yellow precipitate: $K_3Co(NO_2)_6$.</td></tr>
</table>

* A small proportion of the nickel and cobalt present always dissolves in the dilute HCl.

Procedure 67.—*Separation of Zinc from the Nickel and Cobalt.*—Transfer the H_2S precipitate (P. 66) with the filter to a casserole, and add 10–30 cc. 1-normal HCl. Stir the cold mixture frequently for 5 minutes, and filter. Wash the residue and treat it by P. 68.

Boil the HCl solution until the H_2S is completely expelled, add NaOH solution until the mixture is slightly alkaline, transfer it to a casserole, cool, and add 0.5–1 cc. Na_2O_2 powder, a small portion at a time. Boil for several minutes to decompose the excess of Na_2O_2, cool the mixture, and filter. Wash the precipitate thoroly, and treat it by P. 68, uniting it with the sulfide residue undissolved by the dilute HCl. Acidify the filtrate with HAc, and test it for ZINC by P. 57.

Notes.—1. This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate owing to its having been carried down in the Na_2O_2 precipitate, as described in P. 52, Note 6. A small proportion of the nickel and cobalt present (5–20%) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate these elements from the zinc. This Na_2O_2 separation is satisfactory when, as in this HCl solution, the nickel and cobalt are present in small quantity; for then only an insignificant amount of zinc is carried down with them.

2. This Procedure must always be followed in order to determin whether or not zinc is present in the substance, unless a satisfactory test for it has already been obtained in P. 57, or unless the original Na_2O_2 precipitate (P. 52) was small. In either of these two cases this Procedure may be omitted and the H_2S precipitate (P. 66) treated directly by P. 68.

3. The fact that NiS and CoS do not dissolve readily in 1-normal HCl seems inconsistent with the non-precipitation of nickel and cobalt by H_2S with the copper and tin groups from a solution which is only 0.3 normal in acid. This behavior probably arises from the fact that these sulfides exist in at least two allotropic forms of different solubilities. The form that tends to be produced by direct union of sulfide-ion with nickel-ion or cobalt-ion is soluble in dilute acid. The precipitate produced by $(NH_4)_2S$ consists, however, only in part of this soluble form: it contain also a large proportion (increasing with the time that the precipitate has stood) of a form that is nearly insoluble in dilute acids.

Procedure 68.—*Separation of Nickel and Cobalt.*—Transfer the sulfide residue undissolved by dilute HCl and the thoroly washed Na_2O_2 precipitate (P. 67) with the filters to a casserole, add 5–15 cc. HCl and a few drops HNO_3, warm until the black precipitates are dissolved, and filter off the paper. Evaporate the solution just to dryness, moisten the residue with 12-normal HCl, and evaporate again just to dryness (see Note 2, P. 12.) To the dry residue add just 2.0 cc. 12-normal HCl; and, if it does not all dissolve, warm it gently with constant stirring. Cool, add 10 cc. ether previously saturated with HCl gas, and stir for 1–3 minutes. Filter the mixture through a dry filter, and wash out the filter with 5–10 cc. of the HCl-ether reagent. (Yellow residue, presence of NICKEL; blue or green solution, presence of COBALT.) (Residue P. 69; solution, P. 70.)

Notes.—1. The nickel and cobalt must be present as chlorides in order to be separated by this process. The two evaporations with HCl destroy the nitrate.

2. Even 500 mg. of cobalt or 250 mg. of nickel dissolve in 2 cc. 12-normal HCl on gentle warming. 500 mg. of cobalt then remain in solution on the addition of 10 cc. of the HCl-ether reagent.

3. Even 0.5 mg. of nickel yields a distinct yellow residue; and less than 0.5 mg. of cobalt imparts to the ethereal solution a pronounced blue color or green color (the latter resulting from a combination of the blue color of the cobalt with a yellow color coming from organic impurities). It is therefore unnecessary to try the confirmatory test for cobalt when the ethereal solution is colorless. To secure these results, the HCl-ether reagent must, however, be completely saturated with HCl gas.

4. $CoCl_2$ in aqueous solution is pink, like $Co(NO_3)_2$ or $CoSO_4$, when its concentration is small; but it is blue, even in the cold, when its concentration is very large. It is blue, even when its concentration is only moderately large, in hot solutions, or in cold solutions which contain HCl or other chlorides at a high concentration. It is also blue in organic solvents. The pink color is probably due to the cobalt-ion, which is doubtless hydrated (existing perhaps as $Co(H_2O)_4^{++}$ in analogy with $Co(NH_3)_4^{++}$), and to the hydrated unionized cobalt chloride which results directly from the union of this ion with chloride-ion. The blue color is probably due to anhydrous $CoCl_2$, or to complex anions, like $CoCl_3^-$, which result from the union of it with chloride-ion.

Procedure 69.—*Confirmatory Test for Nickel.*—Pour through the filter containing the residue undissolved by ether (P. 68) 10 cc. water, add 3–5 cc. 10% tartaric acid solution, neutralize with NaOH solution, and add 2 cc. in excess. Pass in H_2S gas for about 1 minute, filter out any precipitate that may form, and saturate the filtrate with H_2S. Filter again if there is a precipitate. (Brown coloration, presence of NICKEL.)

Notes.—1. When an alkaline tartrate solution containing a very little nickel (even 0.1–0.2 mg. in 20 cc.) is saturated with H_2S, a clear brown solution is obtained. With somewhat larger amounts of nickel (10–20 mg.) the liquid is opaque, but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of $Ni(OH)_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with H_2S, so that care must be taken to use an excess of H_2S.

2. This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron; for on leading H_2S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulfides and may be filtered off, yielding a filtrate which, when saturated with H_2S, remains colorless if nickel is absent, but becomes dark brown if it is present in even small amount.

Procedure 70.—*Confirmatory Test for Cobalt.*—Heat the ethereal solution (P. 68) in a casserole till the ether is expelled, either by placing it on a steam-bath, or by floating it in a vessel of nearly boiling water from which the flame has been removed. Then evaporate it just to dryness over a small flame. To the residue add 5 cc. water, a few drops of NaOH solution, 5 cc. HAc, and 30 cc. 3-normal KNO_2 solution; and let the mixture stand ten minutes if no precipitate forms sooner. (Fine yellow precipitate, presence of COBALT.)

Notes.—1. The precipitate is potassium cobaltic nitrite, $3KNO_2.Co(NO_2)_3$, or more properly, potassium cobaltinitrite, $K_3Co(NO_2)_6$, since in solution it dissociates into K^+ and the complex anion $Co(NO_2)_6^{\equiv}$. In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite.

2. The precipitate is somewhat soluble in water, but very difficultly soluble in a concentrated KNO_2 solution, owing to the common-ion effect of the potassium-ion. The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly; but, even when only 0.1–0.2 mg. of cobalt is present, a distinct precipitate results within 10 minutes.

3. Nickelous salts are not oxidized by nitrous acid, and they are not precipitated by KNO_2, unless a very large quantity of nickel is present, in which case a dark-yellow or dark-red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate.

PRECIPITATION AND ANALYSIS OF THE ALKALINE-EARTH GROUP.

TABLE XI.—ANALYSIS OF THE ALKALINE-EARTH GROUP.

<table>
<tr><td colspan="5">AMMONIUM CARBONATE PRECIPITATE: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3.(NH_4)_2CO_3$.
Dissolve in HAc, add NH_4Ac and K_2CrO_4 (P. 82).</td></tr>
<tr><td colspan="2" rowspan="2">Precipitate:
$BaCrO_4$.
Dissolve in HCl, evaporate (P. 83).</td><td colspan="3">Filtrate. *Add NH_4OH and alcohol (P. 84).*</td></tr>
<tr><td rowspan="2">Precipitate:
$SrCrO_4$.
Treat with $(NH_4)_2CO_3$ (P. 85).</td><td colspan="2">Filtrate: Ca and Mg salts.
Add $(NH_4)_2C_2O_4$ (P. 86).</td></tr>
<tr><td>*Test in flame*</td><td rowspan="2">*Add HAc, NH_4Ac, and K_2CrO_4.*</td><td rowspan="2">Precipitate:
CaC_2O_4.
Dissolve in dilute H_2SO_4, add alcohol (P. 87).</td><td rowspan="2">Filtrate.
Add NH_4OH and Na_2HPO_4 (P. 88).</td></tr>
<tr><td rowspan="2">Green color:
Ba.</td><td>Residue: $SrCO_3$.
Dissolve in HAc, add $CaSO_4$.</td></tr>
<tr><td>Precipitate:
$BaCrO_4$.</td><td>Precipitate:
$SrSO_4$.</td><td>Precipitate:
$CaSO_4$.</td><td>Precipitate:
$MgNH_4PO_4$.</td></tr>
</table>

Procedure 81.—*Precipitation of the Alkaline-Earth Group.*—Evaporate the filtrate from the $(NH_4)_2S$ precipitate (P. 51) till salts crystallize out, dilute to a volume of 10 cc., cool, and filter.

To the cold solution add 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. 95% alcohol; and, if a large precipitate results, add 15 cc. more of each of these liquids. Shake the mixture continuously for 10 minutes; or better, let it stand, with frequent shaking, for at least half an hour. (Precipitate, presence of ALKALINE-EARTH ELEMENTS.) Filter, and wash the precipitate with a little $(NH_4)_2CO_3$ reagent, using suction if the precipitate is large. (Precipitate, P. 82; filtrate, P. 91.)

Notes.—1. The filtrate from the $(NH_4)_2S$ precipitate is evaporated in order that the elements of the alkaline-earth group may be precipitated more quickly and more completely. The evaporation also serves to destroy $(NH_4)_2S$ and to coagulate any sulfur that may separate. The volume to which the $(NH_4)_2CO_3$ reagent is added should be 10 cc. If ammonium salts have separated they should be filtered off.

2. The $(NH_4)_2CO_3$ reagent is prepared by dissolving 250 g. freshly powdered ammonium carbonate in 1 liter 6-normal NH_4OH.

3. If the ammonium carbonate and hydroxide were added in only small excess, the precipitation of $CaCO_3$, $SrCO_3$, and $BaCO_3$ would not be complete, and additional tests for small quantities of these elements would have to be made in the filtrate. But, by the use of a concentrated solution of $(NH_4)_2CO_3$ containing a large excess of NH_4OH (so as to diminish the hydrolysis of the carbonate into $(NH_4)^+HCO_3^-$ and NH_4OH), the pre-

cipitation may be made practically complete, owing to the greatly increased concentration of carbonate-ion ($CO_3^=$).

4. When the concentrations of $(NH_4)_2CO_3$ and NH_4OH are sufficiently great, magnesium is in the cold also completely precipitated. The precipitate, which is in this case a double carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$, is, however, fairly soluble in cold water and readily soluble in hot water.

5. From a cold aqueous solution the precipitation of these elements takes place slowly, especially in the case of magnesium and calcium; but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure 0.5 mg. of any of the four elements is detected.

Procedure 82.—*Precipitation of Barium.*—Dissolve the $(NH_4)_2CO_3$ precipitate (P. 81) by pouring repeatedly through the filter a 5–15 cc. portion of hot HAc, and evaporate the solution just to dryness, taking care not to ignite the residue.

Add to the residue 3 cc. HAc, 20 cc. 3-normal NH_4Ac, and 15 cc. water; and heat the solution to boiling in a flask. Measure out 8 cc. 3-normal K_2CrO_4 solution, and add it a few drops at a time, heating and shaking after each addition. Finally, heat the mixture at 90–100° for 1 or 2 minutes, shaking at the same time. If a large precipitate forms, add 3 cc. more of the K_2CrO_4 solution. Filter, even tho the solution appear clear; remove the filtrate, and wash the precipitate thoroly with cold water. (Pale yellow precipitate, presence of BARIUM.) (Precipitate, P. 83; filtrate, P. 84.)

Notes.—1. The solubility in water of the chromates of the alkaline-earth elements increases rapidly in the order, Ba, Sr, Ca, Mg, as shown in the Table on page 124. The difference in solubility of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the procedure 0.5 mg. Ba can be detected, while even 400 mg. Sr giv no precipitate. The amount of K_2CrO_4 added is sufficient to precipitate completely more than 500 mg. of barium.

2. Acetic acid is added to increase the solubility of $SrCrO_4$. By its action the concentration of the chromate-ion is decreased, owing to its conversion partly into hydrochromate-ion and partly into bichromate-ion, according to the reactions:

$$CrO_4^= + H^+ = HCrO_4^-; \text{ and } 2HCrO_4^- = H_2O + Cr_2O_7^=.$$

It is evident that the ratio of the $CrO_4^=$ to the $HCrO_4^-$ concentration must decrease as the H^+ concentration increases. For this reason the presence of an excess of a largely ionized acid (such as HCl or HNO_3) would prevent the precipitation of $BaCrO_4$; but since acetic acid is a slightly ionized acid, and since a large amount of acetate is present, the addition of a considerable excess of acetic acid has but little effect.

3. The K_2CrO_4 is added slowly to the hot solution and the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of K_2CrO_4 is added. This is of importance, since, when much barium is present, as much as 3 mg.

Sr may be carried down completely if the K_2CrO_4 reagent be added quickly. If for any reason the filtrate is turbid after two or three filtrations, the precipitate may be coagulated by boiling gently for 1 or 2 minutes. Vigorous or long-continued boiling is to be avoided, since, owing to loss of acetic acid, $SrCrO_4$ may then separate if much strontium is present. When less than 1 mg. Ba is present it is very difficult to distinguish the faint turbidity in the colored solution; but the pale yellow precipitate can be seen after filtering and washing the K_2CrO_4 out of the filter. The precipitate must be washed thoroly, in order to remove strontium as completely as possible, which otherwise would obscure the flame coloration in the confirmatory test for barium.

Procedure 83.—*Confirmatory Test for Barium.*—Pour repeatedly through the filter containing the K_2CrO_4 precipitate (P. 82) a 5–10 cc. portion of hot HCl, and evaporate the solution just to dryness in a small casserole. Heat a platinum wire having a small loop at one end in a gas flame till it no longer colors the flame, dip it in HCl, touch it to the residue in the casserole, and introduce it again into the flame. (Green color, presence of BARIUM.) If this flame test is inconclusiv, treat the residue by the second paragraph of P. 82, using only one third of the volume of each of the reagents. (Yellow precipitate, presence of BARIUM.)

Notes.—1. When the amount of barium present is very small, only a momentary green color is seen as the yellow sodium color which first appears fades away. The only other elements that color the flame green are copper, boron, and thallium. Strontium givs a crimson and calcium an orange-red color.

2. If a small quantity of $SrCrO_4$ was precipitated in P. 82, owing to the presence of a very large amount of strontium in the substance or owing to failure to follow the directions, it will not again precipitate in this second treatment; for the quantity of strontium now present in the solution is much less than before. A yellow precipitate obtained in this second treatment is therefore conclusiv evidence of the presence of barium.

Procedure 84.—*Precipitation of Strontium.*—To the filtrate from the K_2CrO_4 precipitate (P. 82) in a conical flask add NH_4OH slowly until its color changes from orange to yellow, and then 10 cc. more. Dilute the solution to 65 cc., heat it to about 70°, and add to it 50 cc. 95% alcohol, 5 cc. at a time, shaking for 10–15 seconds after each addition if a precipitate forms. Cool the solution in running water, shaking it continuously. If a large precipitate forms, add 3 cc. 3-normal K_2CrO_4 solution and 10 cc. 95% alcohol, and shake. (Light yellow precipitate, presence of STRONTIUM.) Filter after 5–10 minutes with the aid of suction; suck the precipitate as dry as possible, but do not wash it. (Precipitate, P. 85; filtrate, P. 86.)

Notes.—1. Under these conditions 1 mg. of strontium yields a precipitate, while even 400–500 mg. of calcium or magnesium do not do so. A moderate change in the conditions will not affect this result; but if the concentration of alcohol or K_2CrO_4 is much less than is recommended, the precipitation of strontium may be incomplete; while the addition of larger amounts of alcohol and K_2CrO_4 may cause the precipitation of chromate of calcium or magnesium if much of these elements is present, or of K_2CrO_4 itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore always be tried.

2. When a large quantity of strontium or barium is present, the K_2CrO_4 added in P. 82 may have been so far removed from the solution that the strontium is not at first completely precipitated. In such cases, in order to ensure its complete precipitation, more K_2CrO_4 is added in this Procedure.

3. The alcohol is added to the hot solution, in small portions, and with vigorous shaking, so that all the $SrCrO_4$ may not be suddenly precipitated, whereby it is apt to separate in so fine a form that it passes through the pores of the filter-paper.

4. If the filtrate is not perfectly clear, even after a second filtration, it may be made so by adding some paper-pulp, shaking vigorously for a minute or two, and again filtering with the aid of suction. The pulp may be made by shaking violently a filter-paper torn into small pieces with 10 cc. water in a stoppered test-tube, and pressing out most of the water between the fingers.

5. The precipitate is not washed, since $SrCrO_4$ is fairly soluble in water.

Procedure 85.—*Confirmatory Test for Strontium.*—If the K_2CrO_4 precipitate (P. 84) is small, pour three or four times through the filter containing it a hot mixture consisting of 10 cc. $(NH_4)_2CO_3$ reagent and 5 cc. 3-normal K_2CrO_4 solution. If the K_2CrO_4 precipitate is large, transfer it to a casserole, heat it for 4–5 minutes with 15 cc. of the same mixture, and filter. In either case wash the residue thoroly with cold water. Then pour repeatedly through the filter a cold 5–10 cc. portion of 1-normal HAc. Evaporate the solution just to dryness, add 2–3 cc. water, transfer the solution to a test-tube (pouring it through a very small filter, if it is not perfectly clear), add 3 cc. saturated $CaSO_4.2H_2O$ solution, and heat in a vessel of boiling water for at least ten minutes. (Fine white precipitate, presence of STRONTIUM.)

Note.—The mixture of $(NH_4)_2CO_3$ and K_2CrO_4 converts $SrCrO_4$ into the less soluble $SrCO_3$; but it has no action on any $BaCrO_4$ that may be present, and only very little of any such $BaCrO_4$ dissolves in the subsequent treatment with HAc. Any $CaCrO_4$ present is converted by the mixture into $CaCO_3$, and this dissolves in the HAc; but a solution of a calcium salt givs no precipitate with saturated $CaSO_4$ solution (tho it might, of course, do so with a concentrated solution of another sulfate, like K_2SO_4).

Procedure 86.—*Precipitation of Calcium.*—To the filtrate from the K_2CrO_4 precipitate (P. 84) add 60 cc. water, heat it to boiling, add to it slowly 60 cc. boiling-hot $(NH_4)_2C_2O_4$ solution, and keep it nearly boiling for 5 minutes. (White precipitate, presence of CALCIUM.)

Filter the mixture while it is still hot; and wash the precipitate once or twice with water. (Precipitate, P. 87; filtrate, P. 88.)

Notes.—1. The solution is heated to boiling and the ammonium oxalate solution is added slowly, in order to cause the CaC_2O_4 to precipitate in the form of coarser particles which can be more readily filtered. The mixture is kept hot for 5 minutes to ensure the complete precipitation of calcium.

2. The mixture is not heated for more than 5 minutes and is filtered while still hot, in order to prevent so far as possible the precipitation of $MgC_2O_4.2H_2O$. This substance, tho slightly soluble even in hot water, has an unusually great tendency to remain in supersaturated solution, especially if agitation of the solution be avoided. When a large quantity (200–500 mg.) of magnesium is present, it may precipitate even when the above-given directions are closely adhered to.

2. Owing to the possibility that the oxalate precipitate may consist of magnesium or strontium oxalate the confirmatory test for calcium described in P. 87 should always be made.

Procedure 87.—*Confirmatory Test for Calcium.*—Pour repeatedly through the filter containing the $(NH_4)_2C_2O_4$ precipitate (P. 86) a cold 5 cc. portion of H_2SO_4; add 10–15 cc. 95% alcohol, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

Notes.—1. $CaC_2O_4.H_2O$ is very difficultly soluble in water, but dissolves in dilute solutions of largely ionized acids, owing to the formation by metathesis of unionized $HC_2O_4^-$. $CaSO_4$ is somewhat soluble in dilute H_2SO_4, but is completely thrown out as a flocculent precipitate by the addition of the alcohol.

2. One milligram of calcium produces a turbidity at once, 0.5 mg. in 1–3 minutes, and 0.2 mg. within 10 minutes. Even a large amount of magnesium does not interfere with the test. If strontium were present, a small amount of it would dissolve in the H_2SO_4, but only enough to giv a slight turbidity on the addition of alcohol, corresponding to that given by 0.2–0.3 mg. of calcium after standing a few minutes. Therefore anything more than a slight turbidity is a conclusiv proof of the presence of calcium.

Procedure 88.—*Detection of Magnesium.*—To the filtrate from the $(NH_4)_2C_2O_4$ precipitate (P. 86) add 10 cc. 15–normal NH_4OH and 25 cc. Na_2HPO_4 solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.) Filter out the precipitate, wash it once with alcohol, and treat it by P. 89.

Note.—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate, $Mg(NH_4)PO_4$. This salt is fairly soluble even in cold water, owing chiefly to hydrolysis into NH_4OH and $Mg^{++}HPO_4^{-}$; and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature, the solution is cooled to the room temperature, or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mg. of magnesium produces a distinct turbidity in a solution containing 190 cc. water and 50 cc. alcohol within half an hour. A small precipitate of this kind settles out on further standing and may then be detected by rotating the solution so as to cause the precipitate to collect in the center.

Procedure 89.—*Confirmatory Test for Magnesium.*—Pour repeatedly through the filter containing the Na_2HPO_4 precipitate (P. 88) a 5 cc. portion of 2-normal H_2SO_4; add to the solution 20 cc. 95% alcohol, and shake it continuously for two or three minutes. Filter, if there is a precipitate; add to the filtrate 10 cc. water, 20 cc. NH_4OH, and 5 cc. Na_2HPO_4 solution; and let the mixture stand at least half an hour. (White crystalline precipitate, presence of MAGNESIUM.)

Notes.—1. This confirmatory test should be tried whenever Na_2HPO_4 produces a small precipitate that is not distinctly crystalline. For, if even a small quantity of strontium or calcium failed to be precipitated in P. 84 or 86, a flocculent precipitate of $Sr_3(PO_4)_2$ or $Ca_3(PO_4)_2$ would come down on the addition of Na_2HPO_4.

2. The addition of H_2SO_4 and alcohol precipitates strontium and calcium so completely that any precipitate (more than a very slight turbidity) produced on adding Na_2HPO_4 to the H_2SO_4 solution can not be due to these elements.

ANALYSIS OF THE ALKALI-GROUP.

TABLE XII.—ANALYSIS OF THE ALKALI-GROUP.

FILTRATE FROM AMMONIUM CARBONATE PRECIPITATE: NH_4, K, Na salts.
Evaporate and ignite the residue (P. 91).

Vapor: NH_4 salts.	Residue: KCl, NaCl. *Add $HClO_4$, evaporate, add alcohol (P. 92).*		
	Residue: $KClO_4$. *Dissolve in hot water, add $Na_3Co(NO_2)_6$ (P. 93).*	Solution: $NaClO_4$. *Saturate with HCl gas (P. 94).*	
	Yellow precipitate: $K_2NaCo(NO_2)_6$.	Precipitate: NaCl. *Dissolve in water, add $K_2H_2Sb_2O_7$ (P. 95).*	Filtrate: *Reject.*
		Crystalline precipitate: $Na_2H_2Sb_2O_7$.	

Procedure 91.—*Removal of Sulfate and of Ammonium Salts.*—Evaporate the filtrate from the $(NH_4)_2CO_3$ precipitate (P. 81) to a volume of 10–15 cc. till it no longer smells of ammonia.

To 10 drops of the filtrate add 4–5 drops HCl and 1–2 cc. $BaCl_2$ solution. (White precipitate, presence of SULFATE.)

If $BaCl_2$ produces no precipitate, treat the rest of the filtrate by the last paragraph of this Procedure.

If $BaCl_2$ produces a precipitate, add to the rest of the filtrate 5–10 cc. $BaCl_2$ solution, heat the mixture to boiling, and filter out the precipitate. To the filtrate add 5–15 cc. $(NH_4)_2CO_3$ reagent, heat the mixture to boiling, filter out the precipitate, and treat the filtrate by the last paragraph of this Procedure.

Evaporate the filtrate to dryness in a small casserole, and ignite the residue, at first gently, then just below redness, until no more white fumes come off, keeping the dish in motion over a flame and taking care to heat the sides as well as the bottom of the dish. Cool completely, add 5 cc. water, filter the mixture through a 5-cm. filter, evaporate the filtrate to dryness in a small casserole, and heat the dish at a temperature just below redness. (White residue, presence of POTASSIUM or SODIUM.) Treat the residue by P. 92.

Notes.—1. If sulfate is present, either because it was a constituent of the substance or because H_2SO_4 was used in the preparation of the solution (in P. 5 or P. 8), it must be removed before attempting to separate potassium and sodium by P. 92. The process of removing it involves its precipitation as $BaSO_4$ by the addition of $BaCl_2$, the removal of the excess of barium by the subsequent addition of $(NH_4)_2CO_3$, and finally the volatilization of the ammonium salts by ignition. If phosphate is present, it is also removed by the addition of $BaCl_2$ to the neutral solution; but, as it is not necessary to remove it, the preliminary test with $BaCl_2$ is made in HCl solution, in which case sulfate alone produces a precipitate.

2. Great care must be taken to volatilize the ammonium salts completely, since even 1 mg. of ammonium would giv a precipitate in the subsequent test for potassium in P. 92. To ensure their removal the residue is ignited twice. The dish must not, however, be allowed to become red-hot during the ignition, since at that temperature potassium and sodium chlorides are somewhat volatil.

3. The formation of a precipitate with $BaCl_2$ does not necessarily show that sulfate is present in the original substance, even when H_2SO_4 has not been used in preparing the solution; for it may have been produced by the oxidation of sulfide, when the substance contains it, in preparing the solution in P. 3 and 4; or it may even be formed in small quantity by the oxidation of the H_2S and $(NH_4)_2S$ used as reagents.

4. A brown or black residue of organic matter, coming from impurity in the ammonium salts added in the course of analysis and from the alcohol and filter paper, may remain upon treating the ignited residue with water. There may also be a white residue of silica, coming from the action of the reagents on the glass and porcelain vessels throughout the course of the analysis.

5. Since in the dry form even a residue that seems very small may correspond to an appreciable quantity of potassium or sodium, the subsequent tests for these elements should be made if there is any residue whatever after the final ignition.

Procedure 92.—*Separation of Potassium and Sodium.*—To the ignited residue (P. 91) add 5–15 cc. 2-normal $HClO_4$; and evaporate, by keeping the dish in motion over a small flame, till thick white fumes of $HClO_4$ come off copiously (which occurs when the liquid is reduced to about one-fourth of its original volume). Cool completely, add 10–20 cc. 95% alcohol, and stir the mixture for 2–5 minutes if there is much residue. If there is still a residue, add 3 cc. 2-normal $HClO_4$. (White residue, presence of POTASSIUM.) Filter through a dry filter-paper, and wash the residue with 95% alcohol. (Precipitate, P. 93; filtrate, P. 94.)

Notes.—1. Enough $HClO_4$ must be added to convert the potassium and sodium chlorides completely into perchlorates, and the evaporation must be continued till all the HCl is expelled; for otherwise NaCl, being insoluble in alcohol, may be left as a residue with the $KClO_4$. An unnecessary excess of $HClO_4$ is, however, to be avoided, since it makes the subsequent test for sodium somewhat less delicate. The quantity added is therefore varied (from 5 to 15 cc.) in accordance with the size of the ignited residue obtained in P. 91.

2. The evaporation is continued till the $HClO_4$ fumes strongly, also for the purpose of removing most of the water; for this test for potassium and the subsequent test for sodium (in P. 94) are more delicate, the less the quantity of water present. When the directions given in the Procedure are followed, 1–1½ mg. of potassium produces a distinct precipitate.

3. If sulfate were present in the $(NH_4)_2CO_3$ filtrate and it were not removed

in P. 91 by the addition of $BaCl_2$, this separation of potassium and sodium would be unsatisfactory; for, when sodium is present, Na_2SO_4 would remain in the residue undissolved by the alcohol. This arises from the fact that H_2SO_4 is less volatil than $HClO_4$ and is therefore not expelled by it in the evaporation, and from the fact that Na_2SO_4 is only slightly soluble in alcohol even in the presence of $HClO_4$. The presence of phosphate or borate does not, however, interfere with the separation; for, tho phosphoric and boric acids are not volatilized in the evaporation with $HClO_4$ and tho their sodium salts are very slightly soluble in pure alcohol, yet these salts are metathesized by the excess of perchloric acid, since this acid is much more largely ionized than phosphoric or boric acid. The sodium therefore remains dissolved in the alcoholic solution.

4. A small quantity of sulfate is usually produced when the $(NH_4)_2CO_3$ filtrate is evaporated to dryness and the residue is ignited, owing to the action of the nitrate present on sulfur-compounds coming from the decomposition of the $(NH_4)_2S$ reagent. To redissolve any precipitate of Na_2SO_4 arising from this small quantity of sulfate, 3 cc. more of 2-normal $HClO_4$ are added at the end of the Procedure when there is a residue undissolved by the alcohol.

Procedure 93.—*Confirmatory Test for Potassium.*—Pour repeatedly through the filter containing the $HClO_4$ precipitate (P. 92) a 5–10 cc. portion of boiling water, add to the solution 3–5 cc. $NaNO_2$ solution and 2–3 cc. HAc, and boil the mixture gently in a casserole for 5–6 minutes. Cool the mixture, add to it 5 cc. $Na_3Co(NO_2)_6$ reagent, and let it stand for 10 minutes. (Yellow precipitate, presence of POTASSIUM.)

Notes.—1. This confirmatory test should not be omitted, owing to the possibility that, in consequence of imperfect manipulation, the residue left undissolved by the alcohol in P. 92 consists of NH_4ClO_4, NaCl, or Na_2SO_4. The NH_4ClO_4 may result from incomplete removal of the ammonium salts in the ignition, the NaCl from incomplete conversion of the chlorides into perchlorates in the evaporation with $HClO_4$, and the Na_2SO_4 from the presence of sulfate which was not removed by the use of $BaCl_2$.

2. The boiling with $NaNO_2$ and HAc serves to destroy any small quantity of ammonium (up to 20–30 mg.) which might possibly have escaped volatilization in the ignition. It is destroyed in virtue of the reaction $NH_4^+Cl^- + HNO_2 = N_2 + 2H_2O + H^+Cl^-$. If ammonium is present in the solution tested with $Na_3Co(NO_2)_6$, it yields a precipitate closely resembling that produced by potassium.

3. By this test the presence of 0.3 mg. of potassium may be detected within 5–10 minutes. The yellow color of the precipitate can be best seen by collecting it on a filter, and washing out the solution thoroly with cold water.

Procedure 94.—*Detection of Sodium.*—Pour the alcoholic filtrate (P. 92) into a dry conical flask placed in a vessel of cold water, and pass into it a fairly rapid current of dry HCl gas until the gas is no longer absorbed. (White precipitate, presence of SODIUM.) Filter. Reject the filtrate; wash the precipitate with a little alcohol, and treat it by P. 95.

Notes.—1. This test for sodium is most delicate when the alcohol is completely saturated with HCl gas, in which case 1 mg. of sodium can be detected.

2. The dry HCl gas may be prepared by dropping 96% H_2SO_4 from a separating funnel into a flask containing solid NaCl covered with 12-normal HCl, and passing the gas through a gas-wash-bottle containing 96% H_2SO_4. Such a gas-generator may be conveniently kept ready for use in a hood in the laboratory, as the evolution of gas soon ceases when no more H_2SO_4 is added.

3. The alcoholic filtrate containing the excess of $HClO_4$ must not be evaporated, since a dangerous explosion is likely to result.

Procedure 95.—*Confirmatory Test for Sodium.*—Pour a 5–10 cc. portion of water repeatedly through the filter containing the HCl precipitate (P. 94), evaporate the solution just to dryness, add 1 cc. water and 2 cc. $K_2H_2Sb_2O_7$ reagent, pour the mixture into a test-tube, and let it stand for at least half an hour, preferably over night. (White crystalline precipitate, presence of SODIUM.)

Notes.—1. The sodium pyroantimonate ($Na_2H_2Sb_2O_7$) separates as a heavy crystalline precipitate, which usually adheres in part to the glass in the form of distinct crystals, which can be best seen by inverting the test-tube. The test is not extremely delicate; but 1 mg. of sodium is easily detected.

2. With the antimonate reagent many other elements, even if present in small quantity, giv precipitates; thus a distinct turbidity is produced by even 0.1–0.2 mg. of calcium, barium, or magnesium, and by 1–2 mg. of aluminum. These elements produce, however, light, flocculent precipitates which look very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. The crystals of the sodium salt may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle, and decanting off the solution containing the flocculent precipitate in suspension.

SUPPLEMENTARY PROCEDURES FOR BASIC CONSTITUENTS.

Procedure 96.—*Detection of Ammonium.*—Place 0.2–0.3 g. of the finely powdered original substance and 2 cc. NaOH solution in a 50 cc. round-bottom flask. Insert a stopper carrying a glass rod around whose end is wound a piece of moist red litmus paper; and heat the mixture nearly to boiling. (Blue coloration of the litmus paper and odor of ammonia, presence of AMMONIUM.)

Confirmatory Test for Ammonium.—If the litmus turns blue or the vapors smell of ammonia, pour into the flask 10 cc. water, insert a stopper fitted with a long, wide delivery tube leading to the bottom of a test-tube placed in a vessel of cold water, and distil slowly till about half the water has passed over. To the distillate add a 10% solution of K_2HgI_4 in 3–normal NaOH drop by drop so long as the precipitate increases. (Orange precipitate, presence of AMMONIUM.)

Notes.—1. Less than 0.2 mg. of ammonium can be detected with litmus paper and by the odor when the test is carried out as described in the first paragraph of the Procedure. The test described in the last paragraph is useful with very small quantities of ammonium as a confirmation, and with larger quantities as a means of better estimating the proportion of it present.

2. The orange precipitate produced by the action of NH_3 on alkaline K_2HgI_4 is a complex compound of the composition $HgO.HgNH_2I$. The test is extremely delicate, a distinct precipitate resulting even with 0.2 mg. NH_4 in 5 cc. solution, and a pronounced yellow color with a much smaller quantity. This fact must be taken into account in estimating the quantity of ammonium present.

Procedure 97.—*Determination of the State of Oxidation of Mercury, Tin, and Iron.*—If mercury, tin, or iron has been found to be present, heat 20–30 cc. 6–normal H_2SO_4 to boiling in a small flask (to expel the air from the solution and flask); drop in 0.3 g. of the finely powdered original substance; and, if solution does not take place at once, boil the mixture for 2–3 minutes, covering the flask loosely with a small watch-glass. Pour 5 cc. portions of the solution (through a filter if it is not clear) into test-tubes containing: *a*, 5 cc. 1–normal HCl (white precipitate, presence of MERCUROUS MERCURY or silver); *b*, 5 cc. $SnCl_2$ solution (white precipitate, presence of MERCURIC MERCURY); *c*, 5 cc. $HgCl_2$ solution (white precipitate, presence of STANNOUS TIN); *d*, 5 cc. $K_3Fe(CN)_6$ solution (blue precipitate, presence of FERROUS IRON); *e*, 5 cc. KSCN solution (red coloration, presence of FERRIC IRON). If a precipitate is produced by HCl in *a*, filter and add the filtrate (instead of fresh portions of the H_2SO_4 solution) to the solutions named under *b* and *c;* and if silver is present in the substance, treat the HCl precipitate with NH_4OH by P. 14.

Notes.—1. If in preparing the solution for the analysis for basic constituents the substance was dissolved in water or cold dilute HNO_3, the state of oxidation of mercury will have been determined by its presence or absence in the HCl and H_2S precipitate. But, if the substance was treated with hot or concentrated HNO_3, any mercurous compound present will have been partly or completely oxidised to the mercuric state.

2. Stannous and ferrous salts oxidise rapidly in the air. Hence, if the tests for them are to be delicate, the contact with the air must be made as short as possible.

3. Ferrous and ferric salts show a different behavior also with $K_4Fe(CN)_6$; the former giving a white precipitate (of $K_2FeFe(CN)_6$) which rapidly turns blue in the air and the latter a dark-blue precipitate (of ferric ferrocyanide, $Fe_4(FeC_6N_6)_3$). Since this reagent produces a precipitate with both kinds of salts, it is less suitable than $K_3Fe(CN)_6$ for distinguishing between them.—The precipitate produced by $K_3Fe(CN)_6$ with ferrous salts is also ferric ferrocyanide.

Procedure 98.—*Determination of the State of Oxidation of Arsenic.*—If arsenic has been found to be present, place 0.3 g. of the solid substance in a 100 cc. round-bottom flask arranged for distillation as described in P. 111. Place in the receiving flask 50 cc. of water. Pour into the distilling flask 10 cc. 12-normal HCl and distil till about 5 cc. have passed over. (See Note 1.) Pass H_2S into the distillate. (Yellow precipitate, presence of ARSENITE.)

If H_2S produces no precipitate, pour into the distilling flask 5 cc. 12-normal HCl in which 0.5 g. powdered $FeSO_4$ has been dissolved, and distil into a fresh 50 cc. portion of water till 5 cc. have passed over. Pass H_2S into the distillate. (Yellow precipitate, presence of ARSENATE.)

Notes.—1. *As the arsenic vapors are very poisonous, care must be taken that they do not escape into the air.*

2. This method of distinguishing arsenite and arsenate depends upon the facts that arsenite is largely converted by strong HCl into $AsCl_3$, which is volatil with steam, while arsenate is not converted into the corresponding chloride, and is therefore not volatil. By the addition of $FeSO_4$, however, arsenate is reduced in the presence of HCl to $AsCl_3$, which then volatilises with the steam.—Less than 1 mg. of arsenic in either state of oxidation is readily detected by this procedure.

3. When arsenite is present, it can be completely driven over into the distillate by distilling the substance with 10 cc. 12-normal HCl till only 2–3 cc. remain, replacing the HCl which has distilled off, distilling again, and repeating these operations till the distillate givs no precipitate with H_2S. Then, to test for arsenate, a solution of $FeSO_4$ in HCl may be added, the mixture again distilled, and the distillate saturated with H_2S. The removal of the arsenite, is, however, so slow that six or eight repetitions of the distillation may be necessary.

Procedure 99.—*Detection of Very Small Quantities of Arsenic and Antimony.*—Prepare a H_2SO_4 solution of the substance by heating 0.2–0.3 g. of it with 10 cc. H_2SO_4 if it does not contain organic matter, or by treating a larger quantity of it by the first paragraph of P. 8 if it contains organic matter. Place 2–3 cc. of pure, finely granulated zinc in a 75-cc. flask fitted with a stopper through which pass a thistle-tube and a delivery-tube bent at a right angle. Connect the delivery-tube through a tube filled with small lumps of $CaCl_2$ with a hard-glass tube drawn out to a point at one end and constricted to a fairly wide capillary tube in the middle. Pour into the flask 10–15 cc. water and 10–12 drops of $CuSO_4$ solution; then add enough H_2SO_4 to produce a fairly rapid evolution of hydrogen. After the air has been expelled from the apparatus (as shown by the fact that, on filling an inverted 7–cm. test-tube with the gas and touching the mouth of it to a gas-flame, the gas burns quietly without exploding) light the gas at the end of the hard-glass tube and heat that tube just back of the capillary with a small gas flame. (See Note 4.) If after 2–3 minutes no black deposit appears in the capillary (showing the purity of the reagents), pour into the flask the H_2SO_4 solution of the substance, a little at a time, and let the gas continue to pass through the heated tube for 4–5 minutes. (Black deposit in the capillary, presence of ARSENIC or ANTIMONY.) Cool the hard-glass tube, and dip the capillary part of it in a test-tube containing NaOCl solution. (Partial or complete solution of the deposit, presence of ARSENIC; incomplete solution of the deposit, presence of ANTIMONY.)

Notes.—1. This method of detecting arsenic and antimony depends upon the facts that, when hydrogen is produced in a solution containing these elements all of the arsenic is converted into hydrogen arsenide gas (AsH_3) and a part of the antimony is converted into hydrogen antimonide gas (SbH_3); and that these gases decompose into their elements at a moderately high temperature.

2. The treatment of the deposit with NaOCl solution serves to distinguish the two elements; for metallic arsenic is readily converted into H_3AsO_4 by that reagent, while metallic antimony is not acted upon by it. Even when they are present together, it is usually possible to detect both of them; for arsenic, being more volatil, deposits in the part of the capillary further from the flame, and this part of the deposit may be seen to dissolve, and the other part to remain undissolved, in the treatment with NaOCl solution.

3. The addition of the $CuSO_4$ solution serves to produce a deposit of copper on the zinc granules and thus to accelerate through the voltaic action the evolution of hydrogen and the formation of the AsH_3 and SbH_3.

4. Hydrogen arsenide is an extremely poisonous gas. Therefore it must not be allowed to escape into the air through leaks in the apparatus or by discontinuing the heating of the hard-glass tube while much AsH_3 is being evolved.

5. This process is commonly employed for the detection of arsenic in papers, fabrics, and other organic materials.

DETECTION OF THE ACIDIC CONSTITUENTS.

GENERAL DISCUSSION.

The acidic constituents whose detection is here provided for are:

Carbonate.
Sulfite.
Thiosulfate.
Nitrite.
Hypochlorite.
Sulfide.
Cyanide.
Chloride.
Bromide.
Iodide.
Thiocyanate.
Chlorate.
Bromate.
Nitrate.
Phosphate.
Sulfate.
Borate.
Fluoride.

Somewhat different processes are described in this book for the detection of these constituents, according as the substance is:

(1) completely dissolved by cold dilute acids;

(2) decomposed only by hot concentrated acids;

(3) not decomposed even by concentrated acids.

In the process employed when the substance is dissolved by cold dilute acids, certain volatil constituents, namely, carbonate, nitrite, hypochlorite, and chlorate, are first tested for by treating the substance with hot dilute hydrochloric acid and bringing suitable solutions in the form of a drop or upon a test-paper into contact with the vapors. This process is outlined in Table XIII on page 97. A nitric acid solution of the substance is then prepared; and, by adding to portions of it various reagents, most of the other acidic constituents are detected through the formation of characteristic precipitates or colorations. This process is outlined in Tables XIV and XV on pages 98 and 100. The remaining constituents are finally tested for with samples of the original substance, as outlined in Table XIX on page 112.

In the process employed when the substance is decomposed only by hot concentrated acids the substance is first boiled with a solution of phosphoric acid. The vapors which come off while the phosphoric acid is dilute contain the readily volatil constituents; these are condensed in barium hydroxide solution, constituting the "first distillate." The vapors passing over when the phosphoric acid becomes more concentrated contain the acids corresponding to the less volatil constituents, namely, to chloride, bromide, iodide, thiocyanate, chlorate, and nitrate; these are condensed in water, constituting the "second distillate." Finally when the phosphoric acid has become very concentrated, copper is added to it, causing sulfate to be reduced to sulfite and to pass over as sulfurous acid into the "third distillate." These distillates are then tested for the separate constituents by appropriate reagents. This system of procedure is summarized in Tables XVII and XVIII on pages 107 and 110. Portions of the solid substance are then tested for the remaining constituents by such of the procedures outlined in Table XIX on page 112 as the results of the previous tests make necessary.

The second of these processes can, of course, be employed, in place of the first one, also with substances which are dissolved by cold dilute acids; and the analyst may prefer to use it as the general procedure for all substances decomposable by acids.

In the process employed with substances not completely decomposed even by hot concentrated acids, samples of the solid substance are tested for the readily volatil constituents, and portions of a nitric acid extract of the substance are tested for the other constituents, just as in the case of substances dissolved completely by dilute nitric acid. The residue undissolved by nitric acid is then fused with sodium carbonate, the mass is extracted with water, and the solution is tested for the constituents that are likely to be present in insoluble substances, namely, for sulfate, sulfide, chloride, phosphate, borate, and fluoride.

It is to be noted that the system of procedure for detecting the acidic constituents can often be much shortened by omitting the tests for certain constituents which are excluded by the known character or source of the substance, or by its solubility considered in connection with the basic constituents present. Thus, it is useless to test a mineral for nitrite, sulfite, hypochlorite, chlorate, or cyanide; or, in a neutral water-soluble substance containing barium or silver it is unnecessary to test for any of the acidic constituents which form insoluble compounds with these elements. A general statement as to the solubilities of substances in water or dilute acids will be found in Note 9 on page 31; and numerical values of the solubilities of some analytically important substances are given in a table on page 124.

In addition to the acidic constituents listed on page 94, the following ones, which are detected in the course of the analysis for basic constituents, are frequently met with in minerals or industrial products:

Silicate.
Stannate.
Arsenate.
Arsenite.
Chromate.
Permanganate.

TREATMENT OF SOLID SUBSTANCES.

Procedure 100.—*General Directions.*—If the substance is completely dissolved by cold dilute HNO_3 (as used in P. 2), test samples of the substance for certain volatil constituents by P. 101. Prepare a solution of the substance by dissolving 2 g. in 30 cc. cold 1-normal HNO_3; test portions of this solution by P. 102–104; and test the remainder of the solution by P. 105, 106, and 107, if in P. 103 halides are found to be present. Test fresh samples of the substance for borate by P. 121 and for nitrate by P. 124; also for nitrite by P. 125 and for hypochlorite by P. 126, if the previous tests show that they may be present.

If the substance is not completely dissolved by cold dilute HNO_3, but is decomposed by hot concentrated acids (as used in P. 3 and 4), treat a 2 g. portion of it by P. 111, and treat the distillates thus obtained as directed in P. 111. Test also fresh samples of the substance for borate, fluoride, and phosphate by P. 121, 122, and 123; also for nitrate, nitrite, hypochlorite, and chlorate by P. 124–127, if the previous tests show that these constituents may be present.

If the substance is not completely decomposed even by concentrated acids, treat samples of the substance by P. 131.

Notes.—1. When the substance is completely decomposed by dilute acids the analysis for acidic constituents can be made by testing for the various constituents in the manner described in the first paragraph of the foregoing Procedure. When, however, the substance is not decomposed by dilute acids, some of the acidic constituents might escape detection if tested for in these ways. With such a substance it is therefore necessary to use a more powerful decomposing agent. Phosphoric acid is suitable for this purpose, since it is a fairly strong acid whose solution can be made highly concentrated without causing much volatilization or decomposition of the acid. When the substance does not dissolve completely in dilute HNO_3 it is therefore directed to boil it with dilute H_3PO_4 (as described in P. 111) and to condense the vapors which contain all the volatil acids resulting from the decomposition of the substance. This process serves at the same time to separate the acidic constituents of the substance from its basic constituents, thereby facilitating the detection of the acidic constituents.

2. Even with a substance which dissolves completely in dilute acids it is often advantageous to employ the distillation process of P. 111; for tho the tests for the readily volatil acidic constituents described in P. 101 are very delicate, they do not enable a satisfactory estimate to be made of the proportions in which the constituents are present. Moreover, these tests fail to detect certain of the constituents when they are present together (for example, carbonate in the presence of sulfite).

3. If the substance is not decomposed even by hot concentrated acids, it has to be decomposed by fusion with Na_2CO_3, as described in P. 131.

SUBSTANCES DISSOLVED BY DILUTE NITRIC ACID.

TABLE XIII.—DETECTION OF CARBONATE AND OF NITRITE, HYPOCHLORITE, OR CHLORATE.

Heat the substance with H_2O_2 and HCl, and expose to the vapors $Ba(OH)_2$ solution (P. 101).	*Heat the substance with HCl, and expose to the vapors paper wet with starch and KI solutions (P. 101.)*
White turbidity: $BaCO_3$. (Shows CARBONATE.)	Blue coloration: I_2 (Shows NITRITE, HYPOCHLORITE, CHLORATE, BROMATE, OR IODIDE.)

Procedure 101.—*Detection of Carbonate and of Nitrite, Hypochlorite, or Chlorate.*—Place 0.1 g. of the finely powdered substance in a 30 cc. conical flask, add 2 cc. 3% H_2O_2 solution, heat the mixture nearly to boiling, and to the hot mixture add 5 or 6 drops HCl. (Effervescence, presence of CARBONATE.) Insert in the flask a two-hole rubber stopper through which passes a glass rod from which is suspended a drop of $Ba(OH)_2$ solution. (White turbidity, presence of CARBONATE.)

Place in the flask a fresh 0.1 g. sample of the substance, and add to it 2 cc. of water. Make a conical paper-roll out of half a filter-paper; suspend it from the under side of a two-hole rubber stopper by inserting the narrow end of the roll in one of the holes; dip the other end of the roll in a solution of KI and starch contained in a 7-cm. test-tube; drop into the flask 5–6 drops HCl, insert the stopper, and heat the liquid nearly to boiling. (Blue coloration of the paper, presence of NITRITE, HYPOCHLORITE, CHLORATE, BROMATE, or IODIDE.)

Notes.—1. In the test for carbonate H_2O_2 solution is added to oxidise sulfite or thiosulfate to sulfate and prevent the evolution of SO_2, which like CO_2 produces a white precipitate in $Ba(OH)_2$ solution.

2. A blue coloration of the starch-KI paper shows that there is present in the vapors either free iodin or one of the volatil substances which liberates iodin from KI; namely, chlorin, bromin, or nitrogen dioxide. In the presence of starch, which forms with water a colloidal solution, the iodin is dissolved by the minute starch globules or is adsorbed on their surface; and in this finely divided state it possesses a deep blue color. Chlorin or bromin usually arises from the presence in the substance of hypochlorite, chlorate, or bromate, together with a chloride or bromide. Iodin vapors may be liberated from an iodide, when any oxidizing substance, such as a ferric salt, is also present. Nitrogen dioxide is produced from nitrites; it reacts with KI according to the equation: $NO_2+H_2O+2\ KI = NO+I_2+2\ KOH$. When a blue coloration results the nature and quantity of the constituent in the substance which givs rise to it are more definitly determined by later procedures, as described in the general directions given in P. 100.

TABLE XIV.—DETECTION OF THE ACIDIC CONSTITUENTS PRECIPITATED FROM ACID SOLUTIONS BY BARIUM AND SILVER SALTS.

<table>
<tr><td colspan="4"><i>To a HNO_3 solution of the substance add $BaCl_2$ (P. 102).</i></td><td colspan="3"><i>To a HNO_3 solution of the substance add $Cd(NO_3)_2$ (P. 103).</i></td></tr>
<tr><td rowspan="4">Precipitate: $BaSO_4$. [illegible]ws SULFATE.)</td><td colspan="3">Filtrate. <i>Add Br_2.</i></td><td rowspan="4">Yellow precipitate: CdS. (Shows SULFIDE.)</td><td colspan="2">Filtrate: <i>add $AgNO_3$.</i></td></tr>
<tr><td rowspan="3">Precipitate: $BaSO_4$. (Shows SULFITE.)</td><td colspan="2">Filtrate. <i>Add NH_4Ac.</i></td><td rowspan="3">Precipitate: AgCl, AgBr, AgI, $Ag_2(CN)_2$, AgSCN. (Shows HALIDES, CYANIDE, or THIOCYANATE.)</td><td rowspan="2">Filtrate: $AgClO_3$, $AgBrO_3$. <i>Add H_2SO_3.</i></td></tr>
<tr><td rowspan="2">Yellow precipitate: $BaCrO_4$. (Shows CHROMATE.)</td><td>Filtrate. <i>Add $CaCl_2$.</i></td></tr>
<tr><td>Precipitate: CaF_2. (Shows FLUORIDE.)</td><td>Precipitate: AgCl, AgBr. (Shows CHLORATE or BROMATE.)</td></tr>
</table>

Procedure 102.—*Detection of Sulfate, Sulfite, Chromate, and Fluoride.*—To 10 cc. of the HNO_3 solution (P. 100) add 10 cc. $BaCl_2$ solution, and let the mixture stand in the cold for 5 minutes. (White precipitate, presence of SULFATE.)

Filter the mixture, repeatedly if necessary; add to the filtrate (unless it smells of H_2S) saturated Br_2 solution, 1 cc. at a time, till it is present in excess, and let the mixture stand for 5 minutes. (White precipitate, presence of SULFITE.)

Filter the mixture, repeatedly if necessary, add to the filtrate 5 cc. 3–normal NH_4Ac solution, and let the mixture stand 5 minutes. (Fine yellow precipitate, presence of CHROMATE.)

Filter the mixture, add to the filtrate 10 cc. $CaCl_2$ solution, and let it stand 15 minutes. (White turbidity, presence of FLUORIDE.) Confirm the presence of fluoride by filtering off the precipitate, igniting the filter containing it in a spiral of platinum wire till it is incinerated, and treating the residue by P. 122.

Notes.—1. Of the barium salts the sulfate is the only one that is precipitated by a moderate excess of $BaCl_2$ from a HNO_3 solution as strong as 0.5 normal. From the HAc solution produced by adding to such a HNO_3 solution 1½ times as many equivalents of NH_4Ac the chromate is precipitated completely, and the fluoride is precipitated when more than about 10 mg. of fluorin is present. Sulfite, if it were not previously removed by converting it into sulfate by the addition of Br_2, would also precipitate on the addition of the NH_4Ac. From a neutral solution phosphate, carbonate, and borate are also precipitated; but none of these separates from the HAc solution.

2. Of all the inorganic acidic constituents the fluoride is the only one whose calcium salt is much less soluble in water than its barium salts. BaF_2 is soluble in water to such an extent that under the conditions of the procedure about 10 mg. of fluorin remain in the HAc solution. A precipitate produced by $CaCl_2$ therefore shows fluoride. The precipitate of CaF_2 has, moreover, a characteristic appearance, separating first as a milky turbidity which slowly settles out in flocculent form.

3. The addition of NH_4Ac to the HNO_3 solution may cause the precipitation of other substances than $BaCrO_4$ and BaF_2; namely, of any substances, such as bismuth salts, ferric or aluminum phosphate, silicic acid, which are dissolved by HNO_3 but not by HAc. In such a case the test for chromate is obscured; but fluoride may still be detected in the filtrate with $CaCl_2$.

4. Sulfide and sulfite can not be present together in an acid solution; for they destroy each other with the separation of sulfur. It is therefore useless to test a solution containing H_2S for sulfite; moreover, the sulfur which would be precipitated on adding bromin to such a solution might be mistaken for $BaSO_4$.

Procedure 103.—*Detection of Sulfide, of Halides, and of Chlorate or Bromate.*—To a 5 cc. portion of the HNO_3 solution (P. 100) add 5 cc. $Cd(NO_3)_2$ solution. (Yellow precipitate, presence of SULFIDE.)

Filter out the precipitate; and to the filtrate add 20 cc. of water and 5 cc. $AgNO_3$ solution. (White precipitate, presence of CHLORIDE, CYANIDE, or THIOCYANATE; yellow precipitate, presence of BROMIDE or IODIDE.)

Filter out the precipitate; to the filtrate add a few drops of $AgNO_3$ solution; then add 20 cc. HNO_3 and 5 cc. saturated SO_2 solution, and let the mixture stand for 5 minutes. If there is a precipitate, heat the mixture nearly to boiling. (White precipitate, presence of CHLORATE; yellow precipitate, presence of BROMATE.)

Notes.—1. The presence of sulfide is detected by the test-paper test in P. 101; but its precipitation as CdS enables the amount to be better estimated.

2. All the common silver salts, except the three halides, the cyanide, thiocyanate, and sulfide, are either soluble in water (as are the nitrate, sulfate, chlorate, and fluoride), or dissolve readily in HNO_3 owing to displacement of the weaker acid (as do the phosphate, carbonate, borate, and sulfite). There are, however, some exceptions to the principle that salts of weak acids are readily soluble in a strong acid. Thus Ag_2S does not dissolve in dilute HNO_3 because its solubility in pure water is so extremely small that there is only a very minute concentration of $S^{=}$ ion in the saturated solution, and this can yield, in accordance with the mass-action law, only a relativly small concentration of SH^- and unionized H_2S with the H^+ ion of the HNO_3. Silver cyanide has for another reason a very slight concentration of its anion in its saturated solution; namely, because of the fact that this salt exists in the solution mainly as Ag^+ and $Ag(CN)_2^-$, and scarcely at all as Ag^+ and CN^-.

3. The reduction of chlorate to chloride by the H_2SO_3 is not instantaneous; but it is so rapid that 0.5 mg. ClO_3 in a volume of 60 cc. produces a precipitate in less than 5 minutes.

4. Before the addition of the H_2SO_3 a few drops of $AgNO_3$ are added to make sure that the halides have been completely precipitated. A large quantity of HNO_3 is also added to prevent the precipitation of Ag_2SO_3; and, if a precipitate separates on adding the SO_2 solution, the mixture is heated nearly to boiling to make sure that the precipitate is not Ag_2SO_3.

5. If much bromate is present, some of it is precipitated upon the first addition of $AgNO_3$, along with the silver halides; but some of it also remains in the solution and shows the same behavior as chlorate. In order to distinguish between them, the final precipitate with $AgNO_3$ may be treated as follows: Suspend it in 25 cc. water, pass in H_2S until the mixture is saturated with it, heat to boiling, filter off the precipitated Ag_2S, boil the filtrate till the H_2S is expelled, and test it for bromide and chloride by P. 106.

TABLE XV.—DETECTION OF PHOSPHATE AND THE SEPARATE HALIDES.

To portions of the HNO_3 solution of the substance (P. 100):

Add $(NH_4)_2MoO_4$ (P. 104).	*Add $FeCl_3$ (P. 105).**	*Add NaAc, HAc, $KMnO_4$, and $CHCl_3$ (P. 106).**		
Yellow precipitate: $(NH_4)_3PO_4$. $(MoO_3)_{12}$. (Shows PHOSPHATE.)	Red color: $Fe(SCN)_3$. (Shows THIOCYANATE.)	Chloroform layer, purple: I_2. (Shows IODIDE.)	Water layer: *add H_2SO_4, more $KMnO_4$ and $CHCl_3$.*	
			Chloroform layer, orange: Br_2. (Shows BROMIDE.)	Water layer: *boil out the Br_2, add HNO_3 and $AgNO_3$.*
				Precipitate: AgCl (Shows CHLORIDE.)

* These procedures are followed only in case $AgNO_3$ produces a precipitate in P. 103.

Procedure 104.—*Detection of Phosphate.*—Heat 3 cc. of the HNO_3 solution (P. 100) to boiling, add it to 6 cc. $(NH_4)_2MoO_4$ solution, and let the mixture stand 5 minutes. (Yellow precipitate, presence of PHOSPHATE.)

Note.—1. In order that the test may be delicate, a large proportion of the $(NH_4)_2MoO_4$ must be present to reduce the solubility of the precipitate; and a short time must be allowed for the formation of the complex phosphomolybdate. This is promoted by gentle warming; but in a hot solution arsenate or silicate may giv rise to a similar yellow precipitate, while in the cold the reaction is given only by phosphate. By this test 0.1 mg. PO_4 may be detected.

Procedure 105.—*Detection of Thiocyanate.*—If $AgNO_3$ produced a precipitate (in P. 103), add to 2 cc. of the HNO_3 solution (P. 100) 4–5 drops of $FeCl_3$ solution. (Red color, presence of THIOCYANATE.)

Note.—The red color arises from the formation by metathesis of $Fe(SCN)_3$, a substance whose degree of ionization is relativly small. A distinct reddish-yellow color is produced by 0.1 mg. SCN, a deep-red color by 1 mg. or more. Iodides giv a similar red color to $FeCl_3$ solution.

Procedure 106.—*Detection of the Separate Halides.*—If $AgNO_3$ produced a precipitate (in P. 103), add to the remaining 10 cc. of the HNO_3 solution (P. 100) in a conical flask 3-normal Na_2CO_3 solution, a few drops at a time, till the liquid no longer givs a decided red color to blue litmus-paper. (If too much has been accidentally added, add HNO_3 drop by drop till the solution again reddens blue litmus-paper.) Then add 8 cc. NaAc solution, 2 cc. HAc, and (after filtering out any precipitate) 3 cc. chloroform ($CHCl_3$). Finally add 1% $KMnO_4$ solution, 1 cc. at a time, shaking moderately after each addition, till the aqueous layer becomes pink. (Purple coloration of the chloroform, presence of IODIDE.) Pour the mixture through a moistened filter to remove the chloroform and precipitated MnO_2, and shake the filtrate once or twice with a fresh 10 cc. portion of chloroform to extract all the iodin.

Place the aqueous solution and 3 cc. chloroform in a separating funnel, add 5 cc. H_2SO_4, and 1 cc. 1% $KMnO_4$ solution, unless such an excess is already present, and shake. (Yellow or orange coloration of the chloroform, presence of BROMIDE.)

Transfer the aqueous layer to a casserole, add 5–20 cc. 1% $KMnO_4$ solution, and boil the mixture 3–5 minutes. Filter off the MnO_2, and, if the solution is still pink, add H_2SO_3 solution drop by drop until it is colorless. Dilute the solution to 100 cc., filter if necessary, and add 20 cc. HNO_3 and 5 cc. $AgNO_3$ solution. If a precipitate forms, heat the mixture to about 70°. (White precipitate, presence of CHLORIDE.)

Notes.—1. This separation is based upon the different rates at which $KMnO_4$ sets free by oxidation the three halogens from their salts in a solution of definit hydrogen-ion (H^+) concentration. A dilute solution of acetic acid containing considerable sodium acetate has such a hydrogen-ion concentration that an iodide is immediately oxidized by $KMnO_4$ with liberation of iodin, while bromide and chloride are not oxidized to an appreciable extent in the time required for the operations. When the H^+ concentration is increased by the addition of the prescribed quantity of H_2SO_4, the bromide is oxidized very rapidly, while the rate of the corresponding reaction for the chloride is still so small at room temperature that scarcely any chlorin is set free. Even when the solution is boiled to expel the bromin, only a small fraction of the chloride present is oxidized to chlorin.

2. The rate of any reaction is increased by increasing the concentration of any of the substances that is consumed by it. By writing the ionic equation for the reaction between bromide, permanganate, and any acid, 8 H^+ will be

seen to react with 1 MnO_4^-, thus explaining the great effect of the concentration of the hydrogen-ion on the rate of the reaction.

3. To secure satisfactory results, the directions as to the quantities of the acids added must be followed carefully. The proper quantity of H_2SO_4 is that required to react with all the sodium acetate and to giv in addition an excess equal to about 1 cc. H_2SO_4 per 20 cc. of solution.

4. The yellow color of bromin in 3–5 cc. chloroform enables about 0.5 mg. of it to be detected in this procedure.

5. A very small precipitate of AgCl obtained at the end of the procedure does not necessarily indicate the presence of chloride in the substance, unless the reagents used have been proved to be entirely free from chloride. Even then a very slight precipitate (corresponding to less than 0.1 mg. Cl) may result from a reaction between the permanganate and chloroform. For these reasons a blank test should be made in any doubtful case.

6. Before adding the $AgNO_3$ in the test for chloride the solution is diluted and HNO_3 is added to it, so as to prevent the precipitation of Ag_2SO_4 and Ag_2SO_3. The mixture is heated to make sure that the precipitate is not one of these substances.

7. If HCN, H_2S, or HSCN is present in the solution, it will be expelled or destroyed by the boiling with $KMnO_4$ before the test for chloride is made.

Procedure 107.—*Detection of Cyanide.*—Place what remains of the HNO_3 solution in a casserole; add 1 cc. NaOH solution and 0.5 cc. $FeSO_4$ solution; and boil for one minute. To the hot mixture add HCl, a few drops at a time, until, on shaking, the dark colored precipitate of ferrous and ferric hydroxides is dissolved. Cool the mixture. If a precipitate is not plainly visible, filter, and wash out the filter-paper once with water. (Blue precipitate, presence of CYANIDE.)

Notes.—1. This test is based upon the formation of sodium ferrocyanide by the action of the sodium cyanide on the ferrous hydroxide and upon the reaction which takes place on acidification between this ferrocyanide and the ferric salt which has been produced by the oxygen of the air. As a result of these two reactions, ferric ferrocyanide (Prussian blue) is formed, which is difficultly soluble in dilute HCl.

2. A small precipitate is not readily detected in the hot reddish-yellow solution, but is more easily seen in the cold light-colored solution, especially after standing, or when collected on a filter. If the precipitate on the filter is not dark blue, it should be washed with a little hot, dilute hydrochloric acid. With these precautions, 0.2 mg. CN in the solution tested can be detected.

3. Cyanides may be present in the original substance in the form either of simple or of complex cyanides. The latter are characterized by complex anions (such as $Ag(CN)_2^-$ and $Fe(CN)_6^{----}$). These differ very greatly in their stability towards decomposing agents, the difference depending on the extent to which they are dissociated into the simple ions (Ag^+ and CN^- or Fe^{++} and CN^-). Ferrocyanides, ferricyanides, and cobalticyanides are so slightly dissociated in this way that scarcely any HCN is produced when dilute HCl, HNO_3, or H_2SO_4 is added to their cold solutions; but almost all the other complex cyanides (such as $KAg(CN)_2$ or $K_2Ni(CN)_4$) are readily decomposed by

these acids. The above procedure does not distinguish these different simple and complex cyanides from one another.

4. The following procedure enables 2 mg. cyanide to be detected in the presence of ferro or ferricyanide: Place in a 20 cc. distilling flask provided with a thistle-tube 0.5–1 g. of the original substance, 2 g. powdered $CaCO_3$, and 10 cc. water. Add very gradually through the thistle-tube 2 cc. HCl (enough to decompose some, but not all, of the $CaCO_3$). Allow the gas which is evolved to pass into a small test-tube containing 1 cc. NaOH and 5 cc. water. Finally heat the contents of the flask almost to boiling. Test the NaOH solution for cyanide by P. 107.—This separation depends upon the fact that HCN is displaced by H_2CO_3 from simple cyanides and from the relativly unstable complex cyanides, such as $Ag(CN)_2^-$ or $Ni(CN)_4^=$, but not from ferro or ferricyanides.

5. Ferrocyanide and ferricyanide may be detected and distinguished from each other when only one of them is present, by adding a ferric salt to one portion of an aqueous or dilute acid solution, and by adding ferrous salt to another portion of the solution. A ferric salt givs a blue precipitate of ferric ferrocyanide with ferrocyanide, but no precipitate with a ferricyanide. A ferrous salt givs the same blue precipitate (of ferric ferrocyanide) with a ferricyanide; but it also givs with a ferrocyanide a precipitate (of ferrous ferrocyanide), which is white if no ferric salt is present, but which rapidly turns blue in contact with the air.

6. Ferrocyanide and ferricyanide may be detected in the presence of each other by proceeding as follows: Add to an aqueous or dilute HNO_3 solution of the substance $AgNO_3$ and then a moderate excess of NH_4OH. (White precipitate insoluble in NH_4OH, presence of FERROCYANIDE. Orange to red precipitate readily soluble in NH_4OH, presence of FERRICYANIDE.) Filter out and wash the precipitate, and pour over it a little $FeCl_3$ solution. (Blue coloration, presence of FERROCYANIDE.) Acidify the ammoniacal filtrate with HAc, filter out and wash the precipitate, and pour through the filter containing it a little $FeSO_4$ solution. (Orange-red precipitate, which is turned blue by the $FeSO_4$, presence of FERRICYANIDE). This procedure enables 0.2 mg. $Fe(CN)_6$ as either ferro or ferricyanide to be detected when present alone; but the test for ferricyanide is much less delicate in the presence of much ferrocyanide.

SUBSTANCES DECOMPOSED ONLY BY CONCENTRATED ACIDS.

TABLE XVI.—BEHAVIOR OF THE ACIDIC CONSTITUENTS ON DISTILLATION WITH PHOSPHORIC ACID.

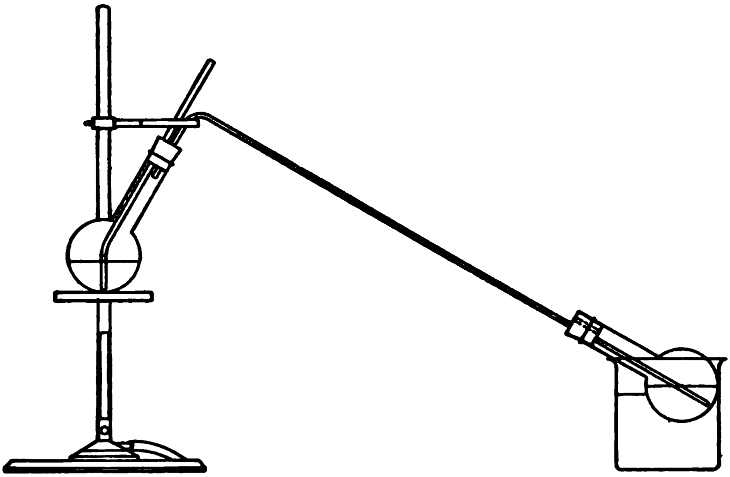
Distil the substance with dilute H_3PO_4 (P. 111). Collect the first half of the distillate in $Ba(OH)_2$ solution and the second half in water. To the residue add Cu and distil again, collecting this third distillate in water.

FIRST DISTILLATE	SECOND DISTILLATE	THIRD DIST.	NONVOLATIL RESIDUE
CO_2 from carbonate. SO_2 from sulfite or thiosulfate. Cl_2 from hypochlorite, chlorate, or chloride.* Br_2 from bromate or bromide.* I_2 from iodide.* HNO_2 from nitrite. H_2S from sulfide. HCN from cyanide. S from sulfide or thiosulfate.	HCl from chloride. HBr from bromide. HI from iodide. HSCN from thiocyanate. HCN from ferro- or ferri-cyanide. H_2S from insoluble sulfides. HNO_3 from nitrate. Cl_2 from chlorate or chloride.* Br_2 from bromide.* I_2 from iodide. S from sulfide, etc.	SO_2 from sulfate.	HPO_3 from phosphate. HBO_2 from borate. H_2SiO_3 from silicate.

* When the substance contains also an oxidizing compound.

Procedure 111.—*Distillation with Phosphoric Acid.*—Place 2 g. of the finely powdered substance and a few glass beads in a distillation-apparatus, arranged as shown in the figure, consisting of a 100 cc. round-bottom hard-glass flask fitted with a rubber stopper, through which pass a delivery tube and a safety-tube, 20–30 cm. long, leading to the bottom of the flask. Support the flask in an inclined position. Lead the end of the delivery tube through a two-hole stopper into 40 cc. of nearly saturated $Ba(OH)_2$ solution contained in a 100 cc. flask supported in a large beaker of cold water. Boil in a small flask for about a minute a mixture of 25 cc. water and 10 cc. 85% H_3PO_4 (to expel any CO_2 present in it). Pour this mixture into the distilling flask with the aid of a small funnel connected with the safety-tube. Heat the mixture to boiling, distil till about 10 cc. have passed over, and then remove the distillate. (White precipitate, presence of CARBONATE, SULFITE, THIOSULFATE, SULFIDE, or SULFUR.)

Cool the distillate, and add to it HAc, 1 cc. at a time, till it reddens blue litmus-paper. (Complete or partial solution of the precipitate or



effervescence, presence of CARBONATE; residue, presence in the substance of free SULFUR, SULFIDE, SULFITE, or THIOSULFATE.) If there is a residue, treat one-third of the distillate immediately by P. 112, and separate portions of the remainder by P. 113, 114, and 115. If there is no residue, treat separate portions of the whole distillate by P. 113, 114, and 115.

Introduce the end of the delivery tube of the distilling flask into another receiving flask containing 35 cc. water. Continue the distillation until the liquid becomes sirupy, boils more quietly, and begins to giv off fine white fumes. Treat this distillate as directed in P. 116.

To the contents of the distilling flask, while still warm, add 5–10 g. of copper filings or turnings. Distil for 3–5 minutes longer, collecting the distillate in 15 cc. of water. Note the odor of the distillate, and treat it by P. 119.

Notes.—1. It is necessary to use a hard-glass flask, since one of ordinary glass is quickly destroyed by the action of hot, concentrated H_3PO_4. The boiling is sometimes violent, especially when much insoluble material is present. The addition of the glass beads serves to reduce the bumping; and placing the flask in an inclined position prevents material from being thrown over into the distillate, which would lead to error in the subsequent tests. In any case in which it seems possible that some of the boiling liquid has been thrown over into the distillate, a small portion of the latter should be tested for phosphate by acidifying it with HNO_3 and adding an equal volume of $(NH_4)_2MoO_4$ solution (see P. 104).

2. Phosphoric acid, which is ionized into H^+ and $H_2PO_4^-$ to a moderate extent (about 40% in 0.1 normal solution), displaces almost completely from their salts (unless these are very difficultly soluble) the much less ionized acids,

H_2CO_3, HNO_2, H_2S, $HClO$, HCN, HF, and H_3BO_3, and also to a large extent the moderately ionized H_2SO_3. Since all these acids, except HF and H_3BO_3, volatilize readily out of aqueous solution, they pass over almost or quite completely into the first distillate, HClO in the presence of chloride giving Cl_2. The largely ionized acids, HCl, HBr, HI, HSCN, HNO_3, $HClO_3$, $H_3Fe(CN)_6$, and $H_4Fe(CN)_6$, are not found in any considerable proportion in the first distillate, since the unionized acid is formed in much smaller proportion, and since in addition it is much less volatil. Of these the first five pass over unchanged and almost completely into the second distillate; for after the H_3PO_4 has become fairly concentrated, the acids are displaced to a greater extent and volatilize more readily in consequence of the higher temperature at which the mixture boils and the smaller proportion of water it contains. From the stronger H_3PO_4 solution HF also passes over in large quantity; but this is not true of H_3BO_3 and H_2SO_4, which volatilize only in insignificant amounts even when the acid has become nearly anhydrous. The three acids, $HClO_3$, $H_4Fe(CN)_6$, and $H_3Fe(CN)_6$, are not volatil as such, but are decomposed by the H_3PO_4 after it becomes fairly concentrated—$HClO_3$ with formation of Cl_2 and O_2, $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ with formation of free HCN. In regard to the acids that may be present in the two distillates, see also Table XVI.

3. The barium salts of all the acids passing into the first distillate, except the carbonate and sulfite, remain in solution. Phosphoric acid, if thrown over mechanically, would, however, also giv a precipitate. Sulfur, when present in the free state or when liberated from a polysulfide or thiosulfate, volatilizes with the steam, and givs a turbid appearance to the water condensed in the delivery tube and to the barium hydroxide solution, by which it is little acted on in the cold. Chlorin is converted by the barium hydroxide into barium chloride and hypochlorite; bromin, into bromide and hypobromite, and into bromide and bromate; and iodin, mainly into iodate and iodide.

4. On acidifying the first distillate slightly with HAc, $BaCO_3$ dissolves, but $BaSO_3$ does not. This difference in behavior is due to the fact that hydrocarbonate-ion (HCO_3^-) is much less ionized than hydrosulfite-ion (HSO_3^-). Sulfur, if present, also remains undissolved. The addition of HAc causes the liberation almost at once of chlorin, bromin, or iodin from a mixture of hypochlorite and chloride, hypobromite and bromide, or iodate and iodide; but bromin is set free somewhat more slowly from a mixture of bromate and bromide.

5. A small precipitate obtained in this procedure (or in the following one) does not prove the presence of carbonate in the mixture unless the prescribed precautions are carefully observed—namely, the boiling of the original H_3PO_4 solution, and avoiding the exposure to the air of the various solutions, especially that of the BaO_2H_2. Even with these precautions, however, it is seldom possible to prevent the absorption of enough CO_2 to produce a slight turbidity.

6. Upon boiling the H_3PO_4 with the copper, H_2SO_4, if present, is reduced to H_2SO_3; and this passes over into the distillate in the form of SO_2 gas. Less than 1 mg. SO_4 can be detected by this process of distillation. The copper should be finely divided and should be added while the liquid is still warm, since on cooling it solidifies to a glassy mass, which consists of pyrophosphoric acid ($H_4P_2O_7$). The heating should be continued for 5–10 minutes; but, if much more prolonged, the contents of the flask change to a solid mass, owing to conversion of the pyro to metaphosphoric acid (HPO_3), which can afterwards be removed only with difficulty, best by heating with HNO_3.

TABLE XVII.—ANALYSIS OF THE FIRST DISTILLATE.

<table>
<tr><td colspan="6">FIRST DISTILLATE.—Precipitate: $BaCO_3$, $BaSO_3$, S.
Solution: $Ba(ClO)_2$, $Ba(BrO)_2$, $Ba(IO_3)_2$, (with halides); $Ba(NO_2)_2$, BaS, $Ba(CN)_2$.
To the whole mixture add HAc (P. 111).</td></tr>
<tr><td colspan="6">Precipitate: $BaSO_3$, S. Solution: H_2CO_3, Cl_2, Br_2, I_2, HNO_2, H_2S, HCN.
Treat portions of the unfiltered mixture as follows:</td></tr>
<tr><td colspan="3">*Add HCl and filter (P. 112).*</td><td>*Add $CHCl_3$ (P. 113).*</td><td>*Filter, add $Cd(NO_3)_2$ (P. 114).*</td><td>*Heat with NaOH and $FeSO_4$ (P. 115).*</td></tr>
<tr><td rowspan="4">Residue: S. (Shows SULFIDE OR THIOSULFATE.)</td><td colspan="2">Solution. *Add Br_2.*</td><td>Purple color: I_2.†
Orange color: Br_2.‡</td><td rowspan="4">Precipitate: CdS. (Shows SULFIDE.)</td><td>Solution: $Na_4Fe(CN)_6$. Precipitate: $Fe(OH)_{2-3}$. *Add HCl.*</td></tr>
<tr><td>Precipitate: $BaSO_4$.*</td><td>Solution: H_2CO_3.</td><td rowspan="3">*If the $CHCl_3$ is colorless, add KI.* Purple color: I_2. (Shows NITRITE, HYPOCHLORITE, OR CHLORATE.)</td><td rowspan="3">Blue precipitate: $Fe_4(Fe(CN)_6)_3$. (Shows CYANIDE.)</td></tr>
<tr><td colspan="2">*Distil a fresh portion of the substance with H_3PO_4 and H_2O_2, collecting the distillate in $Ba(OH)_2$.*</td></tr>
<tr><td colspan="2">Precipitate: $BaCO_3$. (Shows CARBONATE.)</td></tr>
</table>

* Shows SULFITE OR THIOSULFATE. † Shows IODIDE. ‡ Shows BROMATE OR BROMIDE.

Procedure 112.—*Detection of Sulfite or Thiosulfate and of Carbonate.*—To one-third of the first distillate (P. 111), if there was a residue on adding HAc, add 1–2 cc. HCl. (Residue, presence of free SULFUR, SULFIDE, or THIOSULFATE.) Filter, and add to the filtrate saturated bromin solution till the liquid becomes slightly yellow. (White precipitate, presence of SULFITE or THIOSULFATE.)

If sulfite or thiosulfate is found present, treat a fresh 0.3 g. portion of the substance by the first paragraph of P. 111, replacing however 10 cc. of the water added with the H_3PO_4 by 10 cc. 3% H_2O_2 solution. Acidify the distillate with HAc. (Precipitate which dissolves on adding HAc, presence of CARBONATE.)

Notes.—1. Both sulfite and thiosulfate yield SO_2 on distillation with H_3PO_4; but they are distinguished by the fact that the thiosulfate yields also sulfur, while the sulfite does not. The sulfur remains mainly in the distilling flask until the second part of the distillation, but enough of it may pass over into the first distillate to leave it turbid after the addition of HCl.

2. When sulfite or thiosulfate is present the presence of carbonate (unless the proportion of it is large) cannot be determined by the behavior in P. 111 of the barium precipitate towards HAc. To provide for this case it is directed in this Prodecure to distil a fresh portion of the substance with H_3PO_4 in the presence of H_2O_2, which oxidizes sulfite or thiosulfate to sulfate and prevents any SO_2 from passing over into the distillate.

Procedure 113.—*Detection of Nitrite and Halogen-liberating Constituents.*—To one-fourth of what remains of the first distillate (P. 111), add 1–2 cc. HAc and 2–3 cc. of chloroform, and shake vigorously. (Purple coloration of the chloroform, presence in the distillate of free IODIN; yellow or orange coloration, of free BROMIN.)

If there is no coloration, add 8–10 drops of 0.1-normal KI solution, and shake the mixture. (Purple color, presence in the distillate of CHLORIN or of NITROUS ACID; no color, absence of NITRITE and HYPOCHLORITE in the substance.)

If there is a coloration either before or after the addition of KI, test fresh samples of the original substance for NITRITE, HYPOCHLORITE, CHLORATE, and BROMATE by P. 125, 126, and 127.

Notes.—1. For the reactions between the halogens and barium hydroxide and their re-formation on acidifying with HAc, see P. 111, Notes 3 and 4.

2. The characteristic purple color given to chloroform is so delicate a test that even 0.05 mg. of iodin in the solution tested can be detected by this procedure. Bromin may be detected, but only in the absence of iodin, by the orange or yellow color of the chloroform layer when not less than 0.5 mg. of bromin is present in the solution tested. Chlorin gives no decided color to the chloroform, but causes liberation of iodin on the addition of KI.

3. The free halogens distribute themselves between the chloroform and water layers. In the case of pure bromin or iodin the ratio of the concentration in the chloroform to that in the water layer is very large; and this ratio is almost independent of the concentration, in accordance with the so-called distribution law, which requires that the ratio of the concentrations of a given molecular species, such as Br_2 or I_2, in any two non-miscible solvents be constant. When an iodide, like KI, is also present, as it is in the test for free chlorin and nitrous acid, the proportion of iodin extracted by the chloroform is greatly reduced, since the iodin in the aqueous layer is largely combined with the iodide in the form of the triiodide (KI_3); but it is still sufficient to make the color-test a very delicate one, provided only a few drops of the KI solution have been added.

4. For extracting the halogens from aqueous solutions carbon tetrachloride or carbon bisulfide may be used instead of chloroform; but carbon bisulfide has the disadvantage of being highly inflammable.

5. If the tests described in both paragraphs of this procedure yield negativ results, it shows the absence in the substance of nitrite and hypochlorite, but not of the halides nor of chlorate and bromate, since these constituents may not be decomposed or volatilized till the H_3PO_4 becomes concentrated in the later part of the distillation.

6. If the chloroform assumes a purple color when it is first added to the distillate, it shows the presence in the substance of free iodin, of iodate, or of iodide (from which iodin has been liberated in the distillation by the action of the air or by some oxidizing compound present in the substance). If the chloroform assumes an orange color, it shows the presence in the substance of a bromate, or of a bromide together with some oxidizing compound. In these cases the presence or absence of other halogen-containing constituents and of nitrite has to be determined by the special tests described in P. 125–127.

7. If the chloroform becomes colored only after the KI is added, it shows the presence in the substance of nitrite, hypochlorite, or chlorate (or possibly only of chloride in rare cases where a powerful oxidizing substance, such as MnO_2, $KMnO_4$, or $K_2Cr_2O_7$, is also present). A slight purple coloration on adding KI may also arise from a quantity of bromin too small to giv of itself a noticeable yellow color to the chloroform. Which one of these constituents givs rise to the color has to be determined by the special tests.

8. Nitrous acid liberates iodin from KI owing to its reduction to nitric oxide. A peculiarity of this reaction is that the nitric oxide which is formed by it is rapidly reoxidized by the oxygen of the air to nitrous acid, which then reacts with the iodide, so that a continuous liberation of iodin results. Thus the nitrous acid acts as a catalyzer of the reaction between oxygen and HI. This progressiv liberation of iodin is highly characteristic of nitrous acid, but renders it difficult to estimate the amount of it present.

Procedure 114.—*Detection of Sulfide.*—To one-half of what still remains of the first distillate (P. 111), add 2–3 cc. $Cd(NO_3)_2$ solution. (Yellow precipitate, presence of SULFIDE.)

Note.—A negativ test in the first distillate does not prove the absence of sulfide in the original substance, unless the latter has dissolved completely in the dilute H_3PO_4; for some difficultly soluble sulfides, such as CuS, are decomposed only when the H_3PO_4 becomes concentrated, as it does in the latter part of the distillation. It is therefore directed in P. 116 to test also the second distillate for sulfide.

Procedure 115.—*Detection of Cyanide.*—Treat the remainder of the first distillate by P. 107.

Note.—In regard to the detection of cyanide see the Notes on P. 107. In the H_3PO_4 distillation not only the simple cyanides but also nearly all the complex cyanides are decomposed in the first part of the distillation; but a few very slightly soluble complex cyanides (such as Prussian blue) yield HCN only in the second part of the distillation.

TABLE XVIII.—ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

SECOND DISTILLATE: H_2S, HCN, HSCN, HCl, HBr, HI, Cl_2, Br_2, I_2.					THIRD DISTILLATE: H_2SO_3. *Add HCl, $BaCl_2$, and Br_2 (P. 119).*
To a portion add $AgNO_3$ (P. 116).	*If $AgNO_3$ gives a precipitate, treat portions as follows:*				
	Add $Cd(NO_3)_2$ (P. 114).	*Add $FeCl_3$ and HCl (P. 117).*	*Add $CHCl_3$ (P. 118).*		
Precipitate: AgCl, AgBr, AgI, AgSCN, Ag_2S, $Ag_2(CN)_2$.	Precipitate: CdS. (Shows SULFIDE.)	Red color: $Fe(SCN)_3$. (Shows THIOCYANATE.)	$CHCl_3$ layer: I_2, Br_2, Cl_2.* *If colorless, add KI.*	Water layer: HCl, HBr, HI. *Test for separate* HALIDES *by P. 106.*	Precipitate: $BaSO_4$. (Shows SULFATE.)
			Purple color: I_2. (Shows CHLORATE or CHLORIDE.)		

* Purple coloration shows IODIDE, orange coloration, BROMIDE or BROMATE.

Procedure 116.—*Detection of Constituents Precipitable by Silver Nitrate.*—To one-sixth of the second distillate (P. 111) add 1 cc. HNO_3 and 1 cc. $AgNO_3$ solution. (White precipitate, presence of CHLORIDE, CYANIDE, or THIOCYANATE; yellowish precipitate, presence of BROMIDE or IODIDE; black precipitate, presence of SULFIDE.)

If there is a precipitate, test one-sixth of the second distillate for sulfide by P. 114, another sixth for thiocyanate by P. 117, and the remainder for free halogen and halides by P. 118 followed by P. 106.

If there is no precipitate, reject the whole second distillate.

Notes.—1. As to the solubilities of the various silver salts, see Note 2, P. 103.

2. It is not necessary to test for cyanide in this distillate; for even the insoluble ferro and ferricyanides are decomposed partly, tho not necessarily completely, in the first part of the distillation. It is, however, advisable to test for sulfide unless the substance dissolved completely in the hot dilute H_3PO_4, or unless the $AgNO_3$ precipitate is pure white; for some insoluble sulfides begin to decompose only when the H_3PO_4 becomes concentrated.

Procedure 117.—*Detection of Thiocyanate.*—Dilute a sixth of the second distillate (P. 111) to 5–10 cc., add 2–3 drops of $FeCl_3$ solution and 2–3 drops of HCl. (Red color, presence of THIOCYANATE.)

Notes.—1. The red coloration arises from the formation by metathesis of $Fe(SCN)_3$, a substance whose degree of ionization is relativly small. The HCl is added to reduce the hydrolysis of the $FeCl_3$ and diminish the color imparted by it to the solution.—A distinct reddish-yellow coloration is produced by 0.1 mg. SCN. A deep red color is obtained when 1 mg. or more is present.

2. Since in the distillation with H_3PO_4 thiocyanates are destroyed by oxidizing agents, such as nitrates, it is advisable to apply this test also to a solution of the original substance when oxidizing substances are found present.

Procedure 118.—*Detection of Chlorate, Bromate, and the Halides.*—If $AgNO_3$ gave a precipitate in P. 116, to the remainder of the second distillate in a separating funnel add 2–3 cc. chloroform and shake. (Purple color, presence of IODIDE; orange or yellow color, presence of BROMIDE or BROMATE.)

If the chloroform is colorless, separate it from the aqueous layer; and add to the chloroform layer a few drops of KI solution. (Purple color, probable presence of CHLORATE.) If there is no color, treat the aqueous layer left in the separating funnel by P. 106.

If the chloroform becomes colored either before or after the addition of KI, add to the mixture in the separating funnel enough H_2SO_3 solution to reduce the halogen, draw off the chloroform layer if it is still in the funnel, and treat the aqueous layer by P. 106.

Notes.—1. As to these tests see the notes to P. 113.

2. In the second part of the distillation chlorate or bromate, whether present alone or with a halide, is rapidly decomposed with evolution of Cl_2 or Br_2. Therefore, if free halogen is found present neither in the first nor second distillate, it shows the absence of chlorate or bromate. The presence of Cl_2 or Br_2 in the second distillate does not, however, necessarily indicate chlorate or bromate; for these halogens may be produced from the corresponding halides by the action of some oxidizing substance. The special test for chlorate or bromate described in P. 127 should therefore be tried when, and only when, free halogen is found in either the first or second distillate.

Procedure 119.—*Detection of Sulfate.*—To the third distillate obtained upon heating with copper (P. 111), add 1–2 cc. HCl, 3–5 cc. $BaCl_2$ solution, and saturated Br_2 solution till the liquid becomes yellow. (White precipitate, presence of SULFATE.)

Notes.—1. By the action of copper in the presence of concentrated H_3PO_4 on sulfates (even on the very difficultly soluble $BaSO_4$) SO_2 is formed. This is oxidized by the Br_2 to H_2SO_4, which then precipitates as $BaSO_4$. In this way 1 mg. SO_4 may be detected. Even when this small amount is present in the substance, only a small proportion of it passes into the second distillate.

2. Much H_3PO_4 also passes over into the distillate; and the HCl is added to prevent its precipitation as $BaHPO_4$. Too much HCl must not be added since $BaSO_4$ is appreciably soluble in it.

3. When a sulfide is present which has not already been decomposed, sulfur and H_2S, or sulfur and SO_2, may pass into the third distillate, after the acid has become concentrated. The H_2S may be tested for in a portion of the distillate by P. 114. Owing to the possible formation of SO_2 by the oxidation of sulfur at the high temperature attained at the end of the distillation, the test for sulfate is unreliable if sulfur, undecomposed sulfide, or SO_2 gas is present in the distilling flask at the end of the second part of the distillation. In that case a fresh 0.3 g. sample of the substance should be heated with 10 cc. 2-normal HCl, the mixture filtered, and the filtrate tested for sulfate by adding an equal volume of $BaCl_2$ solution.

SUBSTANCES DECOMPOSED BY COLD DILUTE ACIDS OR BY HOT CONCENTRATED ACIDS: SUPPLEMENTARY PROCEDURES.

TABLE XIX.—SUPPLEMENTARY PROCEDURES FOR DETECTING ACIDIC CONSTITUENTS.

Treat samples of the original substance as follows:

Distil with CH_3OH and H_2SO_4 (P. 121).	*Heat with SiO_2 and $KHSO_4$ (P. 122).*	*Boil with HNO_3, add $(NH_4)_2MoO_4$ (P. 123).*	*Distil with H_2SO_4 and $FeSO_4$ (P. 124).*	*Dissolve in water, introduce into an inverted tube filled with HCl solution of urea (P. 125).*	*Heat with water, HAc, and $PbAc_2$ (P. 126).*	*Dissolve in HNO_3, add $AgNO_3$ (P. 127).*
Distillate: $B(OCH_3)_3$. *Collect in CH_3OH and HCl, and add turmeric.*	Gases evolved: SiF_4 and H_2O. Deposit on cold part of tube: SiO_3H_2. (Shows FLUORIDE.)	Yellow precipitate: $(NH_4)_3PO_4 . 12MoO_3$. (Shows PHOSPHATE.)	Distillate: HNO_2. *Add KI and $CHCl_3$.*		Dark brown precipitate: PbO_2. (Shows HYPOCHLORITE.)	Precipitate: AgCl, etc. *Reject.*
Orange color. (Shows BORATE.)			Purple color: I_2. (Shows NITRATE or NITRITE.)	Gas: N_2. (Shows NITRITE.)		Filtrate: $AgClO_3$. *Add H_2SO_3*
						Precipitate: AgCl. (Shows CHLORATE.)

Procedure 121.—*Detection of Borate.*—Place 1–2 g. of the finely powdered substance and a few glass beads in the distilling apparatus used in P. 111, pour in carefully 3 cc. 96 % H_2SO_4, and (unless the substance has dissolved completely) heat for 3–5 minutes hot enough to cause the H_2SO_4 to fume strongly but not to distil over. Cool completely, pour in carefully 10 cc. methyl alcohol (CH_3OH), mix thoroughly, and distil off most of the alcohol, collecting it in a mixture of 5 cc. CH_3OH and 3 cc. 12-normal HCl. Cool the distillate, and add to it five drops of a saturated solution of tumeric in ethyl alcohol. (Red or orange color, presence of BORATE.)

Notes.—1. The substance, in case it is not dissolved by the cold acid, is first heated strongly with the H_2SO_4 to decompose it and liberate the HBO_2 from it.

2. In the presence of a dehydrating agent like concentrated H_2SO_4 methyl alcohol reacts with boric acid to form methyl borate $B(OCH_3)_3$ which is a readily volatil liquid. The color given by turmeric to a solution of boric acid in methyl alcohol and strong hydrochloric acid is so intense that the test is very delicate if the proportions given are reproduced. The presence of 1 mg. BO_2 in the substance distilled may readily be detected.

3. To estimate the quantity of borate present, the color may be compared with that given by known quantities of borate dissolved in a mixture of 5 drops of the turmeric solution, 3 cc. 12-normal HCl, and 15 cc. CH_3OH. And in

any case where the quantity is so small that the orange shade is not pronounced the color of the distillate should be compared with that of the same mixture containing no borate.

Procedure 122.—*Detection of Fluoride.*—Mix 0.2 g. of the dry, finely powdered substance with twice its weight of powdered $KHSO_4$ and with 10–20 mg. dry, finely powdered or precipitated SiO_2. Blow a thick-walled bulb 1½–2 cm. in diameter at the end of a glass tube of 5–8 mm. bore. Place the mixture in the bulb (not using more of it than will one-third fill the bulb). Heat the bulb carefully until the $KHSO_4$ is melted, taking care that the mixture does not froth up into the tube. Continue to heat the bulb and the lower part of the tube until there is a deposit of a solid substance or of condensed acid 3 or 4 cm. above the bulb. After it has cooled, cut off the tube close to the bulb. Dip the tube several times in water, dry it in a flame, and heat it strongly. (White deposit in the middle part of the tube and etched surface at the lower end, presence of FLUORIDE.)

Notes.—1. This test depends on the following reactions:

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

Some of the HF liberated by the molten $KHSO_4$ volatilizes and takes the silica required for the first reaction from the glass, thus producing the characteristic etched surface in the lower part of the tube. The SiF_4 gas and the water-vapor liberated react in the cooler part of the tube according to the second equation (forming a white ring of solid silicic acid and fluosilicic acid, H_2SiF_6). The reaction is reversed at higher temperatures, so that the deposit may be driven up the tube by heating. This white deposit is the most characteristic part of the test for fluoride. A deposit of SO_3 and H_2SO_4 may also form in the upper part of the tube, and might be mistaken for, or interfere with, the test for small amounts of fluoride, if the final washing with water is omitted. This procedure enables 0.5 mg. F to be easily detected.

2. The test fails with certain minerals which are not decomposed by fusion with $KHSO_4$. Such cases are provided for by the treatment described in P. 131.

3. Fluoride is often tested for by heating the solid substance in a platinum crucible with H_2SO_4 alone and detecting any HF evolved by its etching action on a watch glass coated with wax through which markings have been made. This test has the disadvantage that when silica or silicate is present, which is very often the case in minerals, it is unreliable owing to the conversion of the HF to SiF_4 by the reaction given in Note 1.

Procedure 123.—*Detection of Phosphate.*—Heat 0.2 g. of the finely powdered substance with 5 cc. HNO_3. Filter the mixture if it is not clear, and treat the filtrate by P. 104.

Procedure 124.—*Detection of Nitrate or Nitrite.*—Arrange a distillation-apparatus in the way shown in the figure under P. 111. Place in the distilling flask 0.3 g. of the solid substance, 10 cc.

2-normal $FeSO_4$ solution, and 15 cc. H_2SO_4; and place in the receiving flask a mixture of 20 cc. water and 1 cc. NaOH solution. Distil till only about 5 cc. remain in the distilling flask. Acidify the distillate with H_2SO_4, add 2–3 cc. chloroform, and shake (to make sure that the chloroform remains colorless). Then add 8–10 drops of KI solution, and shake again. (Purple coloration of the chloroform, presence of NITRATE or NITRITE.)

Notes.—1. In this procedure the nitrate is reduced by the $FeSO_4$ to nitric oxide (NO), which passes over as a gas into the receiver, where it is oxidized by the oxygen of the air to HNO_2, which is then absorbed by the NaOH. When the solution is acidified ana KI added, I_2 is liberated by the HNO_2. By this procedure 0.2 mg. NO_3 or NO_2 can be detected.

2. The reaction is highly characteristic for nitrates and nitrites, since other oxidizing substances (for example, chlorin or bromin) which might liberate iodin from potassium iodide are reduced by the $FeSO_4$ to compounds which, even if they pass over into the distillate, have no action on KI. The only substances that may interfere are iodides and thiocyanates; if these are present, they should be removed before the distillation by treating the substance with 10 cc. H_2SO_4, adding solid Ag_2SO_4, shaking, and filtering.

Procedure 125.—*Detection of Nitrite.*—To 0.1 g. of the substance add 1 cc. of water and 4–5 drops of HCl. Fill a 7-cm. test-tube brim-full with a 20% solution of urea in HCl; slide over it a circular rubber disk 20 mm. in diameter and 3 mm. thick (cut from a solid rubber stopper), taking care not to enclose an air-bubble; attach the disk firmly to the mouth of the tube by pressing them together for a moment; invert the tube in a 30-cc. nickel or porcelain crucible half-filled with more of the urea solution; and detach the rubber disk from the mouth of the tube with a stirring rod. Introduce the solution of the substance into the test-tube by means of a small tube which has one end closed with a rubber nipple and the other end drawn out and bent so as to form a small U. Take care not to introduce an air-bubble at the same time. (Formation of gas, presence of NITRITE.)

Notes.—1. The reaction between urea and nitrous acid is

$$CO(NH_2)_2+2HNO_2=CO_2+2N_2+3H_2O.$$

The N_2 is liberated in the form of minute bubbles which collect at the top of the tube. When much CO_2 is produced, it also separates as a gas; but a small quantity remains dissolved in the liquid.

2. This procedure enables 0.1 mg. NO_2 to be detected. The amount of nitrite present may be estimated by making a comparativ test with a known quantity of nitrite.

3. The mixture is acidified before it is introduced into the tube so that any carbonate present may be expelled from it.

4. The halogens, chlorin, bromin, and iodin, when combined with alkali in the form of oxyhalides, decompose urea with evolution of nitrogen, but they do not do so when dissolved in the free state in concentrated HCl. They do not therefore interfere with the test when carried out as above described.

Procedure 126.—*Detection of Hypochlorite.*—To 0.5 g. of the powdered substance add 5 cc. water, and then HAc, a few drops at a time, until the solution is acid. Filter if there is much residue, add 2–3 cc. $PbAc_2$ solution, heat the mixture to boiling, and let it stand for ten minutes. (Brown precipitate, presence of HYPOCHLORITE.)

Notes.—1. Hypochlorites are commonly met with either in alkaline solution or in the form of a powder (for example, in bleaching powder). Since they are prepared by the action of chlorin on alkali, chloride is ordinarily present in nearly equivalent amount. When the solid powder is treated with water, the hypochlorite passes into solution; and from it the unionized HClO is liberated upon the addition of the more largely ionized acetic acid. Chlorin is also formed in such quantity as will satisfy the equilibrium-conditions of the reaction $HClO + Cl^- + H^+ = Cl_2 + H_2O$. When in neutralizing with HAc litmus paper is used, the paper will soon be bleached if hypochlorite is present; but the color at the first instant or on the edges of the bleached portion can usually be observed.

2. This test depends upon the oxidation of the lead salt to lead dioxide (PbO_2) by the hypochlorite. The reaction takes place so slowly in the cold that not less than 10 mg. ClO in 5 cc. solution can be detected at room temperature, even if the mixture be allowed to stand a few minutes. But when the mixture is heated, the limit of detectability is about 0.5 mg. in 5 cc. The solution is acidified with HAc, since oxidation does not take place in the presence of a strong acid, such as HNO_3.

3. Peroxides in alkaline solution react instantaneously with lead salts, forming PbO_2; but this reaction does not take place in the presence of HAc, even on boiling. Therefore in the above procedure a peroxide will not be mistaken for a hypochlorite. Peroxide and hypochlorite, moreover, cannot exist together, since they react very rapidly with formation of oxygen.

4. This test for hypochlorite may be made even more delicately in alkaline solution, provided peroxides are known to be absent. If the solution is only slightly alkaline, a small white precipitate of $Pb(OH)_2$ or $PbCO_3$ is first formed; but this turns brown if hypochlorite is present when the mixture is heated and allowed to stand. The delicacy is of course diminished by the presence of a large amount of $Pb(OH)_2$ or $PbCO_3$; but 1 mg. ClO can be detected in the presence of even 2 or 3 g. of these substances, provided an excess of the lead salt is still present in the solution and the mixture is boiled vigorously, preferably in a casserole.

Procedure 127.—*Detection of Chlorate and Bromate.*—Treat 0.3 g. of the powdered substance in the cold with 50 cc. water and 20 cc. HNO_3. (If hypochlorite is present as shown by P. 126, reduce it by adding $NaAsO_2$ solution in excess.) Treat the mixture by the last two paragraphs of P. 103.

SUBSTANCES NOT DECOMPOSED BY CONCENTRATED ACIDS.

Procedure 131.—*Detection of All the Acidic Constituents.*—Treat two 0.3 g. samples of the powdered substance by P. 101; or treat a 2 g. sample of it by the first two paragraphs of P. 111, testing portions of the distillate thus obtained by P. 112–115.

Treat 2 g. of the very finely powdered substance with 30 cc. of cold 1-normal HNO_3, filter, and wash the residue. Treat portions of the solution by P. 102–106. Separate the residue from the filter, if possible; incinerating the paper, if much residue adheres to it, in a spiral of platinum wire. Transfer the residue (with the ash) to a nickel crucible, and dry it by igniting it gently. Mix it in the crucible with 10–15 g. dry Na_2CO_3. Cover the crucible, and heat it, preferably within a cylindrical jacket of asbestos-paper, over a powerful burner for 15–20 minutes. If a perfectly clear fusion does not result, add more Na_2CO_3, and heat again. Cool, place the crucible in a casserole, boil it with water till the fused mass is disintegrated, and filter, rejecting the residue.

To three-fourths of the filtrate add HNO_3 till it is distinctly acid, then add 5 cc. more, filter if there is a precipitate (of silicic acid), and test portions of the solution for sulfate, fluoride, sulfide, halides, and phosphate, by P. 102, 103, and 104.

Test the remainder of the filtrate for borate by evaporating it to complete dryness, adding 96% H_2SO_4 drop by drop as long as there is effervescence, and treating the mixture by P. 121.

If silicate is present, test a fresh sample of the substance for fluoride by P. 122.

Notes.—1. Fusion with Na_2CO_3 metathesizes nearly all insoluble compounds in the way described in the Notes to P. 7.

2. In minerals or metallurgical products undecomposed by acids, it is usually necessary to test only for silicate, chloride, sulfate, phosphate, borate, and fluoride, since other acidic constituents are scarcely ever present.

3. In the process of fusion changes in the state of oxidation may take place. Thus sulfate may be wholly or partially reduced to sulfide, and sulfide wholly or partially oxidized to sulfate. These two constituents must therefore be distinguished by tests made with the unfused substance, as described in the first part of this Procedure.

APPENDICES

PREPARATION OF THE REAGENTS

ACIDS.

Acetic, 6–normal: Mix 350 cc. 99.5% acid with 650 cc. water.
Hydrochloric, 12–normal: Use the C. P. acid of commerce of s. g. 1.19.
Hydrochloric, 6–normal: Mix 12–normal HCl with an equal volume of water.
Hydrofluoric, 48 percent.: Use the pure acid sold in ceresin bottles.
Nitric, 16–normal: Use the C. P. acid of commerce of s. g. 1.42.
Nitric, 6–normal: Mix 380 cc. HNO_3 (s. g., 1.42) with 620 cc. water.
Perchloric, 2–normal: Use the purest acid of commerce of s. g. 1.12.
Phosphoric, 85 percent.: Use the C.P. acid of commerce.
Sulfuric, 96 percent.: Use the C. P. acid of commerce of s. g. 1.84.
Sulfuric, 6–normal: Pour 96% H_2SO_4 into five volumes of water.
Sulfurous, saturated: Saturate water at 20–25° with SO_2 gas made by dropping 96% H_2SO_4 into hot $NaHSO_3$ solution.
Tartaric, 10 percent.: To 100 g. of the solid add enough water to make 1000 cc. of solution.

BASES.

Ammonium hydroxide, 15–normal: Use the C.P. product of s. g. 0.90.
Ammonium hydroxide, 6–normal: Mix 400 cc. 15–normal NH_4OH with 600 cc. water.
Barium hydroxide, 0.4-normal (approximately): Shake 60 g.—of $Ba(OH)_2.8H_2O$ with 1000 cc. water at room temperature, decant or filter.
Sodium hydroxide, 6–normal: Add to 250 g. NaOH "purified by alcohol" enough water to make the volume 1000 cc.

AMMONIUM SALTS.

Acetate, 3–normal: Mix equal volumes of 6–normal HAc and 6–normal NH_4OH; or dissolve 250 g. of the solid salt in enough water to make the volume 1000 cc.
Carbonate: Dissolve 250 g. freshly powdered ammonium carbonate in 1000 cc. 6–normal NH_4OH, and filter if there is a residue.
Chloride, 1–normal: Add to 54 g. NH_4Cl enough water to make the volume 1000 cc.
Molybdate: Dissolve 75 g. of the pure ammonium molybdate of commerce in 500 cc. water, pour the solution into 500 cc. 6–normal HNO_3, and shake the mixture occasionally till the precipitate is dissolved.
Monosulfide, 6–normal: Pass H_2S gas into 200 cc. 15–normal NH_4OH in a bottle immersed in running water or in iced water until the gas is no longer absorbed; then add 200 cc. 15–normal NH_4OH and enough water to make the volume 1000 cc.

Oxalate, 0.5 normal: Dissolve 35 g. $(NH_4)_2C_2O_4.H_2O$ in 1000 cc. water.

Polysulfide, 6-normal: Digest one liter of ammonium monosulfide with 25 g. flowers of sulfur for some hours and filter.

OTHER SALTS.

Name of Salt	*Formula and formula-weight*	*Concentration*	*Grams per liter*
Barium chloride	$BaCl_2.2H_2O$ (244)	1-normal	120
Cadmium nitrate	$Cd(NO_3)_2.4H_2O$ (308)	1-normal	150
Calcium chloride	$CaCl_2.6H_2O$ (219)	1-normal	110
Calcium sulfate	$CaSO_4.2H_2O$ (172)	saturated	2
Cobalt nitrate	$Co(NO_3)_2.6H_2O$ (291)	1% cobalt	50
Copper sulphate	$CuSO_4.5H_2O$(250)	1-normal	125
Ferric chloride	$FeCl_3.6H_2O$ (270)	1-normal	90
Lead acetate	$Pb(C_2H_3O_2)_2.3H_2O$ (379)	1-normal	190
Mercuric chloride	$HgCl_2$ (271)	0.2-normal	25
Potassium chromate	K_2CrO_4 (194)	3-normal	290
Potassium cyanide	KCN (65)	1-normal	65
Potassium ferricyanide	$K_3Fe(CN)_6$ (329)	1-normal	110
Potassium ferrocyanide	$K_4Fe(CN)_6.3H_2O$ (422)	1-normal	105
Potassium iodide	KI (166)	0.1-normal	17
Potassium nitrite	KNO_2 (85)	3-normal	250
Potassium permanganate	$KMnO_4$ (158)	1-per cent.	10
Potassium thiocyanate	$KSCN$ (97)	1-normal	100
Silver nitrate	$AgNO_3$ (170)	1-normal	170
Sodium acetate	$NaC_2H_3O_2.3H_2O$ (136)	1-normal	135
Sodium arsenite	$NaAsO_2$ (130)	1-normal	130
Sodium carbonate	Na_2CO_3 (106)	3-normal	160
Sodium nitrite	$NaNO_2$(69)	3-normal	210
Sodium phosphate	$Na_2HPO_4.12H_2O$ (358)	1-normal	120

SPECIAL REAGENTS.

Bromin, saturated solution: Shake liquid bromin with water, leaving a small excess of it in contact with the solution.

Ether saturated with HCl: pass dry HCl gas into a bottle of ether immersed in water kept at 10–15°, until a 3 cc. portion of the reagent placed in a test-tube immersed in cold water forms a homogeneous liquid (not two layers) when 3 cc. 4-normal HCl are gradually added to it from a dropper.

Ferrous sulfate, 2-normal: Dissolve 280 g. $FeSO_4.7H_2O$ in 0.6-normal H_2SO_4, and keep in contact with iron nails.

Hydrogen peroxide, 3 per cent.

Magnesium ammonium chloride, 1-normal in $MgCl_2$: Dissolve 100 g. $MgCl_2.6H_2O$ and 100 g. NH_4Cl in water, add 50 cc. 15-normal NH_4OH, and dilute to 1000 cc.

Potassium mercuric iodide, 0.5 normal in K_2HgI_4: Dissolve 115 g. HgI_2 and 80 g. KI in enough water to make the volume 500 cc.; add 500 cc. 6–normal $NaOH$; and decant the solution from any precipitate that may form on standing. Keep this stock solution in the dark.

Potassium pyroantimonate: Add 20 g. of the best commercial salt to 1000 cc. boiling water, boil for a minute or two till nearly all the salt is dissolved, quickly cool the solution, add about 80 cc. 10% KOH solution, and filter.

Sodium cobaltinitrite: Dissolve 250 g. $NaNO_2$ in 500 cc. water, add 150 cc. 6-normal HAc and 25 g. $Co(NO_3)_2.6H_2O$, let the mixture stand over night, filter or decant the solution, and dilute it to one liter.

Stannous chloride, 1-normal: Dissolve 115 g. $SnCl_2.2H_2O$ in 170 cc. 12-normal HCl, dilute to 1000 cc., and keep in bottles containing granulated tin.

Starch and potassium iodide: Rub 20 g. starch to a thin paste with a little water in a mortar, and pour the paste into 1000 cc. boiling water. Boil for five minutes, and pour the liquid through a funnel plugged loosely with cotton wool. Add to the filtrate 10 g. KI and 5 cc. chloroform.

Turmeric: Shake turmeric powder with 95% alcohol and filter.

Urea: Dissolve 200 g. urea in 1000 cc. 6-normal HCl.

SOLID REAGENTS.

Beads (glass).
Bismuth dioxide (sold also as sodium bismuthate).
Borax (anhydrous).
Calcium chloride (dry lumps).
Copper (turnings).
Ferrous sulfate (powder).
Lead (finely granulated).
Potassium chlorate (powder).
Potassium hydrogen sulfate.
Potassium nitrate.
Silica (precipitated).
Silver sulfate.
Sodium carbonate (anhydrous).
Sodium peroxide (in 4 oz. cans).
Tin (finely granulated).
Zinc (finely granulated).

SOLVENTS.

Chloroform.
Ethyl alcohol (95%).
Methyl alcohol (acetone-free).

PREPARATION OF THE TEST-SOLUTIONS.

Of the powdered salt whose formula is given in the middle column of the following table weigh out the number of grams given in the last column, and add enough water (or acid when so stated in the foot-note) to make the volume one liter. To prepare the test-solutions, dilute these stock solutions, which contain 100 mg. of the constituent per cubic centimeter, with nine times the volume of distilled water. In a few cases (indicated by the letter H) where the substance is not sufficiently soluble, the stock solution is made up so as to contain 50 mg. of the constituent per cubic centimeter and must be diluted with four times its volume of water to yield the test-solution.—Since these solutions serve also for the preparation of the "unknown solutions," the purest salts that can be purchased should be employed.

Constituent	*Formula of salt*	*Grams per liter*	*Constituent*	*Formula of salt*	*Grams per liter*
Ag	$AgNO_3$	160	Cr	$CrCl_3$(50%sol'n)	610
Pb	$Pb(NO_3)_2$	160	Zn	$Zn(NO_3)_2$	290
Hg(ous)	$HgNO_3.H_2O$	140(*a*)	Fe(ous)	$FeSO_4.7H_2O$	250H(*f*)
Hg(ic)	$Hg(NO_3)_2$	160(*a*)	Fe(ic)	$Fe(NO_3)_3.9H_2O$	715
Bi	$Bi(NO_3)_3.5H_2O$	230(*b*)	Mn	$Mn(NO_3)_2.6H_2O$	530
Cu	$Cu(NO_3)_2.3H_2O$	380	Ni	$Ni(NO_3).6H_2O$	500
Cd	$Cd(NO_3)_2.4H_2O$	275	Co	$Co(NO_3)_2.6H_2O$	500
As(ous)	As_2O_3	13(*c*)	Ba	$BaCl_2.2H_2O$	180
As(ic)	As_2O_5	150	Sr	$Sr(NO_3)_2$	240
Sb	$SbCl_3$	190(*d*)	Ca	$Ca(NO_3)_2.4H_2O$	590
Sn(ous)	$SnCl_2.2H_2O$	190(*e*)	Mg	$Mg(NO_3)_2.6H_2O$	530H
Sn(ic)	$SnCl_4.3H_2O$	270(*e*)	Na	$NaNO_3$	370
Al	$Al(NO_3)_3.9H_2O$	700H	K	KNO_3	260
CO_3	Na_2CO_3	180	Cl	KCl	210
SO_3	Na_2SO_3	160	Br	KBr	150
SO_4	Na_2SO_4	75H	I	KI	130
ClO	NaOCl	...(*g*)	SCN	KSCN	170
S	$Na_2S.9H_2O$	375H	NO_3	KNO_3	165
CN	KCN	250	ClO_3	$KClO_3$	75H
NO_2	KNO_2	185	PO_4	$Na_2HPO_4.12H_2O$	380
CrO_4	K_2CrO_4	170	PO_4	$Ca_3(PO_4)_2$	160(*b*)
F	HF	...(*h*)			

(*a*) Dissolve in 0.6-normal HNO_3. (*b*) Dissolve in 3-normal HNO_3.

(*c*) Digest with 500 cc. 12-normal HCl; then add 500 cc. water, yielding the test-solution of $AsCl_3$ containing 10 mg. As per cubic centimeter.

(*d*) Dissolve in 6-normal HCl; and, in making the test-solution, dilute with 2-normal HCl.

(*e*) Dissolve in 6-normal HCl.

(*f*) Dissolve in 1-normal H_2SO_4, and keep in contact with iron nails.

(*g*) To 600 cc. of the 3½% solution of commerce add 450 cc. water, yielding the test-solution containing 10 mg. ClO per cubic centimeter.

(*h*) To prepare the test-solution containing 10 mg. F per cubic centimeter, mix 17 cc. 48% HF and 1000 cc. water and keep in ceresin bottles.

UNKNOWN SOLUTIONS.

The "unknown solutions" given to the student should contain the constituents to be tested for in quantities which are definitly known by the instructor. As a rule they may well contain in 10 cc. 300 mg. of one of the constituents, 30 mg. of another of the constituents, and 3 mg. of each of two or three of the remaining constituents of the group in question. Such solutions may be conveniently prepared in advance by mixing in a 250 cc. bottle 60 cc. of the stock solution of the first constituent (or 120 cc. if it is half-strength as shown by an H in the table), 6 cc. of the stock solution of the second constituent (or 12 cc. if half-strength), and 6 cc. of the test-solutions of the other constituents, and diluting with enough water to make the volume 200 cc. Of these "unknown solutions" just 10 cc. should be given out to each student for analysis. When time permits two unknowns being done on any group, the second may well contain only 2 mg. of some of the constituents.

APPARATUS REQUIRED.

Returnable.

4 Lipped Beakers, 120 cc. to 500 cc.
2 Casseroles, 50 cc.
2 Casseroles, 100 cc.
2 Casseroles, 200 cc.
1 Conical Flask, 30 cc.
4 Conical Flasks, 75 cc.
4 Conical Flasks, 200 cc., with 1 two-hole rubber stopper.
1 Conical Flask, 500 cc.
2 Jena Round-Bottom Flasks, 100 cc. with 1 two-hole rubber stopper.
1 Filter Flask, 500 cc., with a one-hole rubber stopper.
1 Flat-Bottom Flask, 750 cc., with a two-hole rubber stopper.
1 Flat-Bottom Flask, 250 cc., with a two-hole rubber stopper.
3 Funnels, 2.5 in.
1 Funnel, 2 in.
1 Thistle-Tube.
4 Watch-Glasses, 3 cm.
2 Watch-Glasses, 7 cm.
2 Watch-Glasses, 10 cm.
12 Test-Tubes, 15 cm.
6 Test-Tubes, 7 cm.
1 Separating Funnel, 100 cc.
1 Graduate, 10 cc.
1 Graduate, 50 cc.
1 Nickel Crucible, 30 cc.
1 Porcelain Mortar and Pestle.
1 Desk Key.
1 Gas Burner (Tirrill).
1 Lamp-Stand and Rings.
1 Filter Stand.
1 Test-Tube Rack.

Not Returnable.

12 Hardened Filters, 5.5 cm.
1 Pkg. Filters, 7 cm.
1 Pkg. Filters, 9 cm.
1 Iron Wire-Gauze, 12x12 cm.
1 Box Labels.
1 Note-Book.
1 Piece Platinum Foil, 2 cm. x 1 cm.
1 Piece Platinum Wire, 10 cm.
1 Horn Spoon (bowl 1 cm. long).
1 Piece Glass Rod, 50 cm. long.
1 Sponge.
2 Towels.
1 Nichrome Triangle.
1 Piece Rubber Tubing, 60 cm. long, 6 mm. bore.
1 Piece Rubber Tubing, 60 cm. long, 4.5 mm. bore.
1 Rubber Nipple.
2 Pieces Glass Tubing, each 75 cm. long, 4 mm. bore.
1 Piece Hard-Glass Tubing, 50 cm. long, 6 mm. bore.
1 Tube Blue Litmus Paper.
1 Tube Red Litmus Paper.
1 Box Matches.
1 Triangular File.
1 Screw Clamp.
1 Test-Tube Brush.

IONIZATION VALUES.

The following table shows approximately the percentage of the substance which is dissociated into its ions in 0.1 normal solution at 25°. In the case of the dibasic acids the value opposit the formula of the acid shows the percentage of the first hydrogen that is dissociated, and that opposit the acid ion (HA^-) shows the percentage of it dissociated (into H^+ and A^- for the case that these two ions are present in equal quantities).

Salts of type B^+A^- (*e. g.*, KNO_3)	84%
Salts of type $B^+_2A^=$ or $B^{++}A^-_2$ (*e. g.*, K_2SO_4 or $BaCl_2$)	73
Salts of type $B^+_3A^{\equiv}$ or $B^{+++}A^-_3$ (*e. g.*, $K_3Fe(CN)_6$ or $AlCl_3$)	65
Salts of type $B^{++}A^=$ (*e. g.*, $MgSO_4$)	40
KOH, NaOH	90
$Ba(OH)_2$	80
NH_4OH	1
HCl, HBr, HI, HSCN, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4, H_2CrO_4	90
H_3PO_4, H_3AsO_4, H_2SO_3, $H_2C_2O_4$, HSO_4^-	20–45
HNO_2, HF	7–9
HAc, $HC_2O_4^-$, HSO_3^-	1–2
H_2S, H_2CO_3, $H_2PO_4^-$, $HCrO_4^-$	0.1–0.2
HBO_2, $HAsO_2$, HCN, HCO_3^-	0.002–0.008
HS^-, $HPO_4^=$	0.0001–0.0002
HOH	0.00,000,02

ATOMIC WEIGHTS OF THE COMMON ELEMENTS.

Aluminum	Al	27.1	Iron	Fe	55.84
Antimony	Sb	120.2	Lead	Pb	207.10
Arsenic	As	74.96	Magnesium	Mg	24.32
Barium	Ba	137.37	Manganese	Mn	54.93
Bismuth	Bi	208.0	Mercury	Hg	200.6
Boron	B	11.0	Molybdenum	Mo	96.0
Bromin	Br	79.92	Nickel	Ni	58.68
Cadmium	Cd	112.40	Nitrogen	N	14.01
Calcium	Ca	40.07	Oxygen	O	16.00
Carbon	C	12.00	Phosphorus	P	31.04
Chlorin	Cl	35.46	Potassium	K	39.10
Chromium	Cr	52.0	Silicon	Si	28.3
Cobalt	Co	58.97	Silver	Ag	107.88
Copper	Cu	63.57	Sodium	Na	23.00
Fluorin	F	19.0	Strontium	Sr	87.63
Gold	Au	197.2	Sulfur	S	32.07
Hydrogen	H	1.008	Tin	Sn	119.0
Iodin	I	126.92	Zinc	Zn	65.37

SOLUBILITIES OF SLIGHTLY SOLUBLE SUBSTANCES.

The numbers in the table show the solubility in milli-equivalents per liter at 20°. The letters v.s. (very soluble) denote a greater solubility than 1-normal. In the case of the carbonates the values have been corrected for hydrolysis so as to correspond to the ion-concentration product in the saturated solution.—For a general statement in regard to the solubilities of other substances, see Note 9, page 31.

	Mg	Ca	Sr	Ba	Pb	Ag
Chloride	v.s.	v.s.	v.s.	v.s.	70.	0.01
Bromide	v.s.	v.s.	v.s.	v.s.	45.	0.0005
Iodide	v.s.	v.s.	v.s.	v.s.	2.6	0.00002
Thiocyanate	v.s.	v.s.	v.s.	v.s.	28.	0.0008
Sulfate	v.s.	30.	1.5	0.02	0.28	50.
Chromate	v.s.	60.	12.	0.03	0.0003	0.16
Carbonate	20.	0.2	0.2	0.2	0.0004	0.2
Hydroxide	0.3	45.	130.	450.	0.2	0.18
Fluoride	2.8	0.4	1.9	18.	5.	v.s.
Oxalate	5.	0.09	0.5	0.8	0.012	0.24
Phosphate	—	0.7	—	—	0.001	0.05

INDEX

In this index the figures in black-face type refer to the Procedures and the figures after them in ordinary type refer to the Notes. Figures in italics preceded by the letter *p* refer to page numbers.

ACETATES, solubility, **2**, 9.
Acidic constituents
  general discussion, *p. 94*.
  list of, *p. 94*.
  procedures, **100–131**.
  tabular outlines, *p. 97, 98, 100, 104, 107, 110, 112*.
Alkali-group
  analysis, procedures, **91–95**.
  analysis, tabular outline, *p. 87*
Alkaline-earth
  chromates, solubility, **82**, 1, 2.
  elements, separation from iron-group, **65**; **66**.
  group analysis, procedures, **81–89**.
  group analysis, tabular outline, *p. 81*.
  phosphates, solubility, **51**, 6.
  salts, solubility, *p. 124*.
Alloys
  action of acids, **3**, 6, 9; **4**, 3.
  preparation of solution, **3**; **4**; **4**, 3, 4.
  pulverization, **3**, 5.
  quantity taken for analysis, **3**, 5.
  residue from acid treatment, **3**, 6, 7, 9.
Aluminum
  detection, **51**, 2, 5; **53**; **54**.
  separation from chromium and zinc, **53**.
  testing of reagents for, **53**, 2.
Aluminum-group
  analysis, procedures, **53–57**.
  analysis, tabular outlines, *p. 65, 71*.
  hydroxides, behavior with ammonium hydroxide, **51**, 4.
  hydroxides, behavior with sodium hydroxide, **52**, 3.
  hydroxides, color, **51**, 2.
  separation from other groups, **51**; **52**.
Ammonium
  decomposition, **93**, 2.
  detection, **1**, 4; **96**.
  monosulfide reagent, **22**, 2.
  phosphomolybdate, **63**, 2; **104**, 1, 2.
  polysulfide reagent, **22**, 2.
  salts, solubility, **2**, 9.
  salts, volatilization, **1**, 4; **91**, 2.
  sulfide, reactions with aluminum and iron groups, **51**, 8.
  sulfide, reactions with copper and tin groups, **22**, 3, 5.
Amphoteric substance
  definition, **36**, 1.
  examples, **36**, 1; **51**, 4.
Antimony
  detection, **3**, 7; **12**; **21**, 2; **44**; **45**; **99**.
  distinction from arsenic, **45**, 3; **99**, 2.
  distinction from copper and mercury, **45**, 1.
  hydrolysis of salts, **2**, 9.
  oxychloride, **12**, 5.
  separation from silver, mercury, lead, **12**.
  separation from tin, **44**.
  solubility, **3**, 6.
  sulfo-salts, **22**, 3.
Apparatus
  care of platinum, **5**, 5.
  for hydrofluoric acid solutions, **5**, 5.
  required, *p. 122*.
Aqua regia, properties, **4**, 1.
Arsenates
  distinction from arsenites, **98**, 2.
  reaction with hydrogen sulfide, **43**, 2, 3.
  separation from arsenites, **98**, 3.
  solubility, **2**, 9.
Arsenic
  detection, **1**, 4; **21**, 2; **42**; **43**; **99**.
  determination of state of oxidation, **98**.
  distinction from antimony, **99**, 2.
  reaction with hydrogen sulfide, **43**, 2, 3.
  separation from antimony and tin, **41**.
  sulfo-salts, **22**, 3.
  volatility of compounds, **1**, 4; **42**, 2; **98**, 2.
Arsenites
  distinction from arsenates, **98**, 2, 3.
  solubility, **2**, 9.
Atomic weights, table, *p. 124*.

BARIUM
  detection, **82**; **83**.
  flame-color, **83**, 1.
  fluoride, distinction from calcium fluoride, **102**, 2.
  fluoride, solubility, *p. 124*.
  hydroxide, reaction with halogens, **111**, 3.
  hydroxide, solubility, **52**, 7; *p. 124*.
  salts, solubility, **102**, 1; **111**, 3, 4; *p. 124*.
  separation from calcium, strontium, magnesium, **82**.
  sulfate, distinction from lead sulfate, **34**, 1, 2.
  sulfate, solubility, **5**, 6; **102**, 1; *p. 124*.
Basic acetate precipitation, **65**; **65**, 2, 3.

Basic constituents
general discussion, *p. 41*.
procedures, 11–99.
separation into groups, *p. 42*.
tabular outlines, *p. 42, 43, 47, 54, 60, 65, 71, 74, 78, 81, 86*.
Bismuth
detection, 12; 21, 2; 35; 36.
hydrolysis of salts, 2, 9.
oxychloride, formation, 12, 4.
oxychloride, solubility, 12, 6.
separation from copper and cadmium, 35.
separation from silver, mercury, lead, 12.
Borates
detection, 2, 6; 83, 1; 121.
effect on alkali-group analysis, 92, 3.
flame-color, 83, 1.
phosphoric-acid distillation, 111, 2.
solubility, 2, 9.
Bromates
detection, 101; 103; 113; 118; 127.
distinction from chlorates, 103, 5.
reaction with bromides, 111, 4.
Bromides
detection, 103; 106; 116; 118.
oxidation by permanganate, 106, 1, 2.
phosphoric-acid distillation, 111, 2.
reaction with bromates, 111, 4.
reaction with hypobromites, 111, 4.
separation from chlorides and iodides, 106.
solubility, 2, 9; *p. 124*.
Bromin
detection, 113.
distribution between water and chloroform, 113, 3.
formation from acidic constituents, 101, 2.
reaction with barium hydroxide, 111, 3.

CADMIUM
detection, 21, 2; 38.
distinction from copper, 37, 1.
formation of complex anions, 38, 3.
formation of complex cations, 35, 2.
reaction with ammonium hydroxide, 35, 2.
separation from lead and mercury, 38, 5.
Calcium
detection, 83, 1; 86; 87.
flame-color, 83, 1.
fluoride, distinction from barium fluoride, 102, 2.
fluoride, solubility, *p. 124*.
oxalate, solubility, 87, 1; *p. 124*.
salts, solubility, *p. 124*.
separation from magnesium, 86.
sulfate, solubility, 87, 1; *p. 124*.
Carbonates
detection, 1, 4; 2, 6, 7; 101; 111; 112
phosphoric-acid distillation, 111, 2.
separation from sulfites, 112, 2.
solubility, 2, 9; *p. 124*.
Chlorates
detection, 1, 4; 101; 103; 113; 118; 127.
distinction from bromates, 103, 5.
phosphoric-acid distillation, 111, 2.
solubility, 2, 9.
Chlorides
detection, 103; 106; 116.
oxidation by permanganate, 106, 1, 2.
phosphoric-acid distillation, 111, 2.
reaction with hypochlorites, 111, 4.
separation from bromides and iodides, 106.
solubility, 2, 9; *p. 124*.
Chlorin
formation from acidic constituents, 101, 2.
reaction with barium hydroxide, 111, 3.
Chromates
detection, 21, 6; 102.
solubility, 82, 1; *p. 124*.
Chromium
detection, 6, 1; 51, 2; 51, 5; 55; 56.
formation of complex cations, 51, 4.
separation from zinc, 55.
Closed-tube test
procedure, 1.
interpretation of results, 1, 2, 3, 4.
Cobalt
detection, 1, 2; 51, 2; 52, 1; 66; 68; 70.
formation of complex cations, 51, 4.
separation from nickel, 68.
separation from zinc, 67.
separation from nickel and zinc, tabular outline, *p. 78*.
sulfide, solubility, 52, 1; 67, 3.
Common-ion effect, principles, 11, 6.
Copper
chloride (cuprous), distinction from mercurous chloride, 32, 1.
detection, 1, 2; 21, 2; 23, 5; 35; 37; 83, 1.
distinction from cadmium, 37, 1.
distinction from nickel, 37, 2.
flame-color, 83, 1.
formation of complex anions, 38, 2.
formation of complex cations, 35, 2.
reaction with ammonium hydroxide 35, 2.
separation from bismuth, 35.
Copper-group
analysis, procedures, 31–38.
analysis, tabular outline, *p. 54*.
separation from tin-group, procedures 21; 22.
separation from tin-group, tabular outline, *p. 47*.

Copper-group
  sulfides, behavior with ammonium sulfide, 22, 5.
  sulfides, color, 21, 2.
  sulfides, effect of acid on precipitation, 21, 4.
Cyanides
  detection, 2, 5, 6, 7; 103; 107; 115; 116.
  forms in which found, 107, 3.
  phosphoric-acid distillation, 111, 2; 115, 1.
  separation from ferricyanides and ferrocyanides, 107, 4.
Distillation
  with phosphoric acid, 111; 111, 1.
  behavior of acids, 111, 2.
Equations, method of balancing, 21, 7.
Equivalent,
  definition, 11, 4.
  metathetical, 11, 4.
  oxidation, 11, 4.
Evaporation, manipulation, 5, 3; 12, 2.
Ferricyanides
  detection, 107, 5, 6. (See also cyanides)
  phosphoric-acid distillation, 111, 2; 115, 1.
  reactions with iron salts, 107, 5.
  separation from ferrocyanides, 107, 6.
Ferrocyanides
  detection, 107, 5, 6. (See also cyanides)
  phosphoric-acid distillation, 111, 2; 115, 1.
  reactions with iron salts, 107, 5.
  separation from ferricyanides, 107, 6.
Filtration by suction, 23, 1.
Flame-colors of various elements, 83, 1.
Fluorides
  detection, 102; 122; 122, 3.
  effect on analysis of aluminum and iron groups, 51, 7.
  phosphoric-acid distillation, 111, 2.
  solubility, *p. 124*.
Fluosilicic acid, properties, 122, 1.
Gold, proof of absence, 3, 9.
Graphite, detection, 4, 3.
Hydrochloric acid
  preparation of gaseous, 94, 2.
  properties, 3, 4; 4, 1.
Hydrofluoric acid, properties, 5, 1, 4, 5.
Hydrogen-ion, sources, 2, 6.
Hydrogen sulfide, precipitation by, 21, 4.
Hydroxide-ion, sources, 2, 6.
Hydroxides
  detection, 2, 5, 6.
  solubility, 2, 9; *p. 124*.
Hypobromites, reaction with bromides, 111, 4.
Hypochlorites
  detection, 101; 113; 126.
  distinction from peroxides, 126, 3.
  phosphoric-acid distillation, 111, 2.
  reaction with chlorides, 111, 4.
  reaction with peroxides, 126, 3.
  sources, 126, 1.
Iodates, reaction with iodides, 111, 4.
Iodides
  detection, 1, 4; 3, 1; 101; 103; 106; 116; 118.
  oxidation by permanganate, 106, 1, 2.
  phosphoric-acid distillation, 111, 2.
  reaction with iodates, 111, 4.
  separation from bromides and chlorides, 106.
  solubility, 2, 9; *p. 124*.
Iodin
  detection, 1, 4; 113.
  distribution between water and chloroform, 113, 3.
  formation from acidic constituents 101, 2.
  reaction with barium hydroxide, 111, 3.
Ionization
  method of indicating, *p. 2*.
  values, table, *p. 123*.
Iron
  detection, 21, 6; 51, 5; 64; 65.
  determination of state of oxidation, 21, 6; 97; 97, 3.
  oxidation of compounds, 51, 2; 97, 2.
  separation from cobalt, nickel, zinc, 64; 65.
Iron-group
  analysis, procedures, 61–70.
  analysis, tabular outlines, *p. 74, 78*.
  hydroxides, color, 51, 2.
  reaction with ammonium hydroxide, 51, 4.
  reaction with sodium hydroxide, 52, 3.
  separation from aluminum-group, procedures, 51; 52.
  separation from aluminum-group. tabular outline, *p. 65*.
  sulfides, color, 51, 9.
Lead
  chloride, solubility, 11, 5; 12, 3; *p. 124*.
  detection, 13; 21, 2; 33; 34.
  formation of complex anions, 12, 3.
  salts, solubility, *p. 124*.
  separation from cadmium, 38, 5.
  separation from bismuth, cadmium, copper, 33.
  separation from mercury and silver, 13.
  sulfate, distinction from barium sulfate, 34, 1.
  sulfate, solubility, 4, 1; 5, 6; 31, 6; 33, 1; 34, 2; *p. 124*.

MAGNESIUM
  ammonium arsenate, properties, 42, 4.
  ammonium phosphate, properties, 88, 1.
  detection, 88; 89.
  salts, solubility, p. *124*.
  separation from calcium, 86.
Manganese
  detection, 61; 62.
  separation from cobalt, iron, nickel, zinc, 61.
  sulfide, color, 51, 9.
  sulfide, oxidation, 51, 9.
Mercury
  determination of state of oxidation, 97.
  salts, hydrolysis, 2, 9.
  salts, solubility, 2, 9.
  salts, volatility, 1, 4.
Mercury (mercuric)
  detection, 1, 4; 21, 2; 23, 5; 32.
  distinction from mercurous, 97.
  formation of complex anions, 12, 3.
  separation from bismuth, cadmium, copper, lead, 31.
  separation from cadmium, 38, 5.
  sulfide, solubility, 4, 1; 31, 1, 3.
Mercury (mercurous)
  chloride, distinction from cuprous chloride, 32, 1.
  chloride, reaction with ammonium hydroxide, 14, 2.
  chloride, solubility, 2, 9; 12, 3.
  detection, 1, 4; 14.
  distinction from mercuric, 97.
  separation from silver, 14.
Minerals, acidic constituents in, 131, 2; p. *95*.

NICKEL
  detection, 1, 2; 51, 2; 52, 1; 66; 68; 69.
  distinction from copper, 37, 2.
  formation of complex cations, 51, 4.
  separation from cobalt, 68.
  separation from zinc, 67.
  separation from cobalt and zinc, tabular outline, p. *78*.
  sulfide, solubility, 52, 1; 67, 3.
Nitrates
  detection, 1, 4; 124.
  distinction from nitrites, 125.
  phosphoric-acid distillation, 111, 2.
  separation from iodides and thiocyanates, 124, 2.
  solubility, 2, 9.
Nitric acid, properties, 3, 4.
Nitrites
  detection, 1, 4; 101; 113; 124; 125.
  phosphoric-acid distillation, 111, 2.
  reaction with potassium iodide, 101, 2; 113, 8.
  reaction with urea, 125, 1.
  solubility, 2, 9.
Note-book records
  experimental operations, p. *2*.
  results of analyses, p. *4*.

ORGANIC MATTER
  detection, 1; 1, 2.
  effect on analysis, 1, 1.
  removal, 8.
Oxalates
  detection, 1, 4.
  solubility, p. *124*.
Oxidation-state
  of arsenic, determination, 98.
  or iron, determination, 97.
  of mercury, determination, 97.
  of sulfur, effect of fusion, 131, 3.
  of tin, determination, 97.

PERCHLORIC ACID, properties, 92, 3; 94, 3.
Permanganates, detection, 21, 6.
Peroxides
  detection, 1, 4; 126, 3.
  distinction from hypochlorites, 126, 3.
  reaction with hypochlorites, 126, 3.
Persulfides, detection, 1, 4.
Phosphates
  detection, 2, 6; 63; 104; 123.
  effect on alkali-group analysis, 92, 3.
  effect on analysis of aluminum and iron groups, 51, 6; 52, 8.
  solubility, 2, 9; 51, 6; p. *124*.
Phosphoric acid, properties, 100, 1; 111, 2.
Phosphoric-acid distillation
  behavior of acidic constituents, 111, 2.
  procedures, 111–119.
  tabular outlines, p. *104*, *107*, *110*.
Platinum
  apparatus, use of, 5, 5; 7, 5.
  proof of absence, 3, 9.
Potassium
  cobaltinitrite, constitution, 70, 1.
  cobaltinitrite, solubility, 70, 2.
  detection, 92; 93.
  salts, solubility, 2, 9.
  separation from sodium, 92.
Precipitates
  ignition, 5, 2.
  production, 42, 4.
  solution, 12, 1; 22, 1.
  washing, 21, 1.

QUANTITATIV estimation of constituents, p. *4*.

REACTION-RATE, principles, 106, 1, 2.
Reagents
  concentration, 11, 3; p. *117–119*.
  definition, p. *41*.
  manipulation, 11, 2; 14, 1; 23, 2.
  preparation, p. *117–119*.
  required, p. *117–119*.

SILICA
  detection, 5.
  presence as impurity, 5, 4; 53, 2.
Silicates, detection, 2, 5; 3, 2; 5.
Silicic acid, properties, 3, 2; 122, 1.
Silicon fluoride
  properties, 5, 4.
  reaction with water, 122, 1.
Silver
  chloride, reaction with ammonium hydroxide, 14, 3.
  chloride, solubility, 4, 1; 12, 3; *p. 124*.
  detection, 2, 5; 14; 15.
  formation of complex anions, 12, 3; 103, 2.
  formation of complex cations, 14, 3.
  salts, solubility, 103, 2; *p. 124*.
  separation from mercury, 14.
Silver-group
  analysis, procedures, 11–15.
  analysis, tabular outline, *p. 43*.
Sodium
  bismuthate, constitution, 62, 3.
  carbonate, fusion with, 7; 7, 1.
  detection, 94; 95.
  hydroxide, reaction with aluminum and iron groups, 52, 3.
  hydroxide, tests for impurities, 53, 2.
  peroxide, reaction with aluminum and iron groups, 52, 4.
  peroxide, tests for impurities, 53, 2.
  pyroantimonate, distinction from other pyroantimonates, 95, 2.
  pyroantimonate, physical properties, 95, 1.
  salts, solubility, 2, 9.
  separation from potassium, 92.
  stannite, amphoteric properties, 36, 1.
  stannite, preparation, 36, 1.
  stannite, reducing power, 36, 2.
Solubility
  general statement, 2, 9.
  of slightly soluble substances, table, *p. 124*.
Solubility-product, definition, 11, 6.
Solution, preparation for analysis, 2–8.
Solvents
  required, *p. 119*.
  treatment with, 12, 1; 22, 1.
Strontium
  detection, 83, 1; 84; 85.
  flame-color, 83, 1.
  salts, solubility, *p. 124*.
  separation from calcium and magnesium, 84.
  sulfate, solubility, 4, 1; 5, 6; *p. 124*.
Sulfates
  conversion into carbonates, 6, 1.
  detection, 102; 119.
  effect on alkali-group analysis, 92, 3.
  effect of fusion, 131, 3.
Sulfates
  reduction, 111, 6; 131, 3.
  solubility, 2, 9; *p. 124*.
Sulfides
  detection, 1, 4; 2, 5, 6, 7; 3, 1; 103; 111; 112; 114; 116.
  effect of fusion, 131, 3.
  phosphoric-acid distillation, 111, 2.
  reaction with sulfites, 102, 4.
Sulfites
  detection, 1, 4; 2, 7; 102; 111; 112.
  distinction from thiosulfates, 112, 1.
  oxidation, 112, 2.
  phosphoric-acid distillation, 111, 2.
  reaction with sulfides, 102, 4.
Sulfo-salts
  of tin-group, formation, 22, 3.
  of tin-group, reaction with acids, 23, 3.
Sulfur
  detection, 1, 4; 2, 5; 111; 111, 3; 112.
  liberation from sulfides, 3, 1.

TEST-SOLUTIONS
  concentration, *p. 2, 120*.
  preparation, *p. 120*.
Thiocyanates
  detection, 103; 105; 116; 117.
  phosphoric-acid distillation, 111, 2.
  solubility, 2, 9; *p. 124*.
Thiosulfates
  detection, 2, 7; 101; 111; 112.
  distinction from sulfites, 112, 1.
  oxidation, 112, 2.
Tin
  detection, 3, 7; 21, 2; 46.
  determination of state of oxidation, 97.
  hydrolysis of salts, 2, 9.
  oxidation of stannous salts, 97, 2.
  separation from antimony, 44.
  solubility, 3, 6.
  sulfo-salts, 22, 3.
Tin-group
  analysis, procedures, 41–46.
  analysis, tabular outline, *p. 60*.
  separation from copper-group, procedures, 21–23.
  separation from copper-group, tabular outline, *p. 47*.
  sulfides, color, 21, 2.
  sulfides, behavior with ammonium sulfide, 22, 5.
  sulfides, effect of acid on precipitation, 21, 4.
  sulfo-salts, formation, 22, 3.
  sulfo-salts, reaction with acids, 23, 3.

UNKNOWN SOLUTIONS, preparation, *p. 121*.
Unknown substances
  preliminary examination, 1.
  preparation for analysis, procedures, 2–8.

Unknown substances
  preparation for analysis, tabular outline, *p. 29.*
  quantity taken for analysis, 2, 2; 3, 5.
Urea, reaction with nitrites, 125, 1.

WATER
  detection, 1; 1, 3.
  forms in which found, 1, 3.

ZINC
  detection, 57.
  formation of complex cations, 51, 4; 53, 1.
  separation from chromium, 55.
  separation from cobalt and nickel, procedure, 67.
  separation from cobalt and nickel, tabular outline, *p. 78.*

STANFORD UNIVERSITY LIBRARY

To avoid fine, this book should be returned on
or before the date last stamped below.

MAY 2 [illegible]

April 24th

JUN 3 1994
JUN 4 1994

544 .N959c
C.1
A course of instruction in the
Stanford University Libraries
3 6105 032 130 176

246106